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(57) Abstract

The present invention relates to skin care compounds and skin care compositions comprising such compounds. In particular, these compounds and compositions comprising such compounds are useful for improving the appearance of dry mammalian skin. These skin care compounds are phenolic hydrophobic, metal ion chelators of defined chemical structure, which have the unique properties of (i) being hydrophobic and (ii) having the ability to bind metal ions. These chelators can optionally be formulated in a dermatologically acceptable carrier. The present invention also encompasses methods of improving the appearance of dry mammalian skin and methods of desquamating mammalian skin by treating dry mammalian skin with the herein-described skin care compounds and/or skin care compositions containing these compounds.

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SKIN CARE COMPOUNDS AND COMPOSITIONS COMPRISING SUCH COMPOUNDS

TECHNICAL FIELD

The present invention relates to skin care compounds, as described herein, and skin care compositions comprising such compounds. In particular, these compounds and compositions comprising such compounds are useful for improving the appearance of dry mammalian skin. These skin care compounds are phenolic hydrophobic, metal ion chelators of defined chemical structure, which have the unique properties of (i) being hydrophobic and (ii) having the ability to bind metal ions. These chelators can optionally be formulated in a dermatologically acceptable carrier. The present invention also encompasses methods of improving the appearance of dry mammalian skin and methods of desquamating mammalian skin by treating dry mammalian skin with the herein-described skin care compounds and/or skin care compositions containing these compounds.

BACKGROUND OF THE INVENTION

Many personal care products or compositions claim to improve the appearance of dry skin which is the single most recognized indicator of poor skin condition. In general, conventional personal care products attempt to provide relief for dry skin appearance by one of the following mechanisms: (i) using occlusive oils to form a film on top of the skin; (ii) using humectants to bind or attract moisture into or onto the skin; and (iii) using desquamatory actives to slough or peel off the outer layer of skin cells and thereby renewing the skin surface. However, these traditional methods of treating dry skin appearance are usually temporary, ineffective, or overly harsh to the skin. In addition, these traditional methods of treating dry skin appearance tend to be messy and, generally, not aesthetically pleasing to the consumer because they require either maintaining an oily/sticky film on the skin for a prolonged period of time or treating the skin with harsh, skin irritating chemical materials.

Therefore, it is seen that conventional methods of treating or improving the appearance of dry skin can be ineffective and unappealing. A need clearly exists to develop personal care products which are effective in providing acceptable improvement of the appearance of dry skin without the negative drawbacks of these conventional personal care products.

It has been surprisingly found in the present invention that phenolic hydrophobic, metal ion chelators, as herein described, and skin care compositions comprising such chelators can dramatically improve the appearance of dry skin. Due to their hydrophobic nature, these chelators penetrate into the superficial layers of the skin while creating virtually no skin irritation. In addition, it is believed that these chelators maintain or enhance the natural desquamation processes of mammalian skin. As a result, the skin is neither treated with harsh chemical compounds to induce unnatural or artificial desquamation (e.g., peeling of skin with retinoic acid or glycolic acid) nor is the consumer required to maintain a sticky or oily film on the skin for a prolonged duration of time.

It is therefore, an object of the present invention to provide skin care compounds which effectively improve the appearance of dry skin.

It is another object of the present invention to provide personal care compositions comprising the skin care compounds of defined chemical structures as hereinafter described.

It is another object of the present invention to provide skin care compounds and personal care compositions containing these compounds which effectively improve the appearance of dry skin without overly irritating the skin.

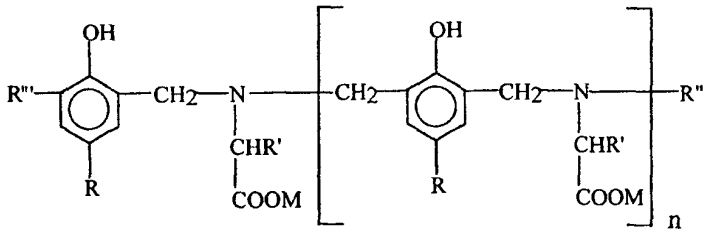
It is another object of the present invention to provide methods for improving the appearance of dry mammalian skin by applying compositions, which contain these skin care compounds of defined structure, onto the skin.

It is another object of the present invention to provide methods of desquamating mammalian skin by applying compositions, which contain these skin care compounds of defined structure, onto the skin.

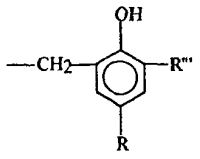
These and other objects of this invention will become apparent in light of the following disclosure.

SUMMARY OF THE INVENTION

The present invention relates to a skin care compound useful for improving the appearance of dry mammalian skin, said compound having the following chemical structure:



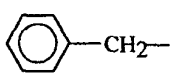
wherein R" is selected from the group consisting of -H or



;

each R is independently selected from the group consisting of C_1-C_{22} alkyl, C_1-C_{22} ester, C_1-C_{22} amide, and C_1-C_{22} ether;

each R' is independently selected from the group consisting of H-, C_1-C_{22} alkyl, HO-CH_2, $CH_3CH(OH)$-, $HSCH_2$-, CH_3-SCH_2CH_2-, H_2NCOCH_2, $H_2NCOCH_2CH_2$-, $HOOCCH_2$-, $HOOCCH_2CH_2$-, and

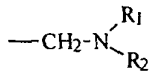


;

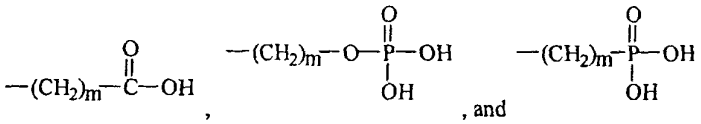
each M is independently selected from the group consisting of H+, C_1-C_{22} alkyl, alkali metal ion, NH_4+, and aluminium ion;

n is an integer from 0 to 6; and

each R''' is independently selected from H or



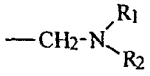
wherein R_1 and R_2 are independently selected from the group consisting of



, and

wherein m is an integer from 1 to 3; and

wherein at least one R''' is



if R is a C_1-C_{22} alkyl.

In further embodiments, the present invention relates to a skin care active component comprising the skin care compounds described herein.

In preferred embodiments, the skin active component has a specific oligomeric content achieved by regulating the n value in the chemical structure. The specific oligomeric content is such that a predominant portion of the skin care active component comprises the skin care compound having $n \geq 2$.

In further embodiments, the present invention relates to methods for obtaining an active component having the defined oligomeric content by synthetic or separation methods.

In further embodiments the present invention relates to topical compositions for improving the appearance of dry skin. These compositions comprise (A) a skin active component comprising the skin care compound, as herein described, and (b) a dermatologically acceptable carrier.

In even further embodiments, the present invention relates to methods of improving the appearance of dry skin. Such methods comprise the step of applying to the skin of a mammal a safe and effective amount of the compounds and/or compositions described herein.

In even further embodiments, the present invention relates to methods of desquamating the skin. Such methods comprise the step of applying to the skin of a mammal a safe and effective amount of the compounds and/or compositions described herein.

All percentages and ratios used herein, unless otherwise indicated, are by weight and all measurements made are at 25°C, unless otherwise designated. The invention hereof can comprise, consist of, or consist essentially of, the essential, as well as, optional ingredients and components described therein.

DETAILED DESCRIPTION OF THE INVENTION

The phenolic hydrophobic, metal ion chelators of the present invention are highly efficacious for improving the appearance of dry skin. The term "appearance of dry skin," as used herein, means the visual and perceived characteristics associated with dry skin. Nonlimiting examples of characteristics associated with dry skin include lack of skin smoothness (rough skin), redness, crackiness, scaliness, and flakiness. These chelators can optionally be formulated into a dermatologically acceptable carrier which can also contain other optional skin active ingredients to further enhance the improvement of the appearance of dry skin.

Without being limited by theory it is believed that these hydrophobic, metal ion chelators effectively penetrate into the superficial layers of the skin and enhance or maintain the normal process of desquamation in mammalian skin. The term "desquamation," as used herein, is meant to describe the natural or unnatural process of removing (e.g., sloughing off) old cells constituting the upper epidermal layer of mammalian skin. This process allows renewal of the upper epidermal layer of mammalian skin by younger differentiated skin cells.

The surface of the epidermal skin layer in mammals consists of a complex matrix of dead skin cells which form a natural barrier function against excessive moisture loss from the skin. In healthy skin, the make up of this complex matrix is constantly changing with the introduction of newly differentiated epidermal cells and the desquamation of old epidermal skin cells. Without being limited by theory, desquamation is believed to be achieved by proteolysis which consists of skin enzymes, such as stratum corneum chymotryptic enzyme (SCCE), cleaving the protein rivets that act as the adhesive connecting the individual differentiated epidermal cells. This results in normal desquamation, an orderly degradation of cell-cell rivets which is imperceptible because individual cells separate and fall off of the surface of the skin. However, in aging or environmentally stressed mammalian skin (e.g., by external environmental factors, such as cold weather), this delicate balance is disrupted. Instead of single cell-cell rivets, clumps of skin cells consisting of numerous cell-cell rivets become visible to the naked eye as flakes of skin. As clumps of epidermal cells separate form the surface of the skin, the natural moisture barrier function of the epidermal layer is compromised and becomes inefficient thereby resulting in dry, flaky, and/or scaly skin.

Further, without being limited by theory, it is believed that, in aging or environmentally stressed mammalian skin, higher than normal levels of calcium bind to the cell-cell rivet thereby protecting it from proteolysis by skin proteins, such as stratum corneum chymotryptic enzyme. It is further believed that the hydrophobic, metal ion chelators described herein effectively remove the calcium from the cell-cell rivets to allow reinitiation of the natural process of proteolysis by the skin proteins. As a result, the natural process of desquamation is reestablished so that the sloughing off of the individual skin cells becomes imperceptible. Eventually, the integrity of the natural moisture barrier function of the epidermal layer is also reestablished.

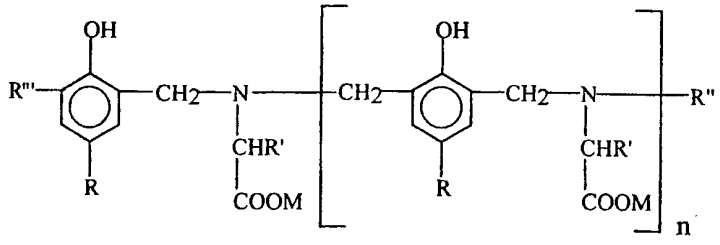
The present invention essentially comprises a phenolic hydrophobic, metal ion chelater as herein described. These skin care compounds can optionally be formulated into a dermatologically acceptable carrier which may also contain optional active ingredients.

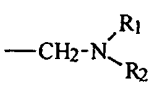
I. PHENOLIC HYDROPHOBIC, METAL ION CHELATOR

The present invention essentially comprises a phenolic hydrophobic, metal ion chelater as hereinafter described. These chelators can optionally be used in skin care composition by formulating them into a dermatologically acceptable carrier. Such skin care compositions encompassed by the present invention essentially comprise a skin active component which comprises the hydrophobic, metal ion chelators hereinafter described. Such compositions of the present invention comprise a sufficient amount of the skin active component to provide from about 0.1% to about 99.5%, preferably from about 0.2% to about 50%, more preferably from about 0.5% to about 25%, and most preferably from about 1% to about 10%, by weight of the composition, of a hydrophobic, metal ion chelator.

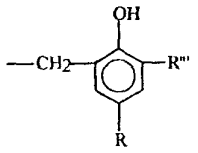
Generally, the hydrophobic, metal ion chelators of the present invention have (i) at least one chemical moiety which has a strong affinity for alkaline earth metal ions, and (ii) at least one lipophilic chemical moiety which is sufficient to render the hydrophobic, metal ion chelator to be soluble in octanol to greater than about 0.5% by weight, preferably greater than about 1% by weight, and more preferably greater than about 1.5% by weight. These chelators should be sufficiently hydrophobic to penetrate into the superficial layers of the skin and also posses sufficient metal-ion chelating characteristics to enhance or maintain the natural process of desquamation in mammalian skin. Chemical moieties, which have strong affinity to alkaline earth metal ions, include, but are not limited to, carboxylates, phosphates, phosphonates, phenols, amines, alcohols, ethers, and combinations thereof. Lipophilic chemical moieties, which have the ability to sufficiently render the hydrophobic, metal ion chelator soluble in octanol to greater than 0.5% by weight, include, but are not limited to, saturated hydrocarbons, unsaturated hydrocarbons, aromatic hydrocarbons, silicones, fluorocarbons, and derivatives and mixtures thereof.

The phenolic hydrophobic, metal ion chelators of the present invention have the following chemical structure:



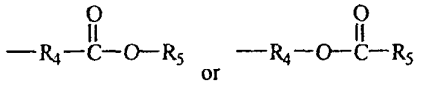
wherein at least one R''' is  if R is a C_1-C_{22} alkyl.

R'' is selected from the group consisting of -H or



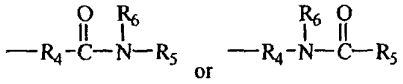
Each R is independently selected from the group consisting of C_1-C_{22} alkyl, C_1-C_{22} ester, C_1-C_{22} amide, and C_1-C_{22} ether. Without being limited by theory, it is believed that these chemical moieties (e.g., C_1-C_{22} esters, C_1-C_{22} amides, and C_1-C_{22} ethers) can confer greater biodegradability to the hydrophobic metal, ion chelators. As a result these chelators and skin care compositions containing these compounds can be more environmentally friendly.

The C_1-C_{22} ester is defined by the following chemical structures:



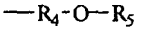
wherein R_4 + R_5 equals to C_2-C_{22} ,and wherein R_4 is selected from the group consisting of straight or branched C_1-C_{18} alkyl, straight or branched C_1-C_{18} alkene, and C_1-C_{18} alkyne, and R_5 is selected from the group consisting of H, straight or branched C_1-C_{18} alkyl, straight or branched C_1-C_{18} alkene, and C_1-C_{18} alkyne.

The C_1-C_{22} amide is defined by the following chemical structures:



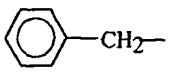
wherein R_4 + R_5 +R_6 equals C_2-C_{22}, and wherein R_4 is selected from the group consisting of straight or branched C_1-C_{18} alkyl, straight or branched C_1-C_{18} alkene, and C_1-C_{18} alkyne, and R_5 and R_6 are independently selected from the group consisting of H, straight or branched C_1-C_{18} alkyl, straight or branched C_1-C_{18} alkene, and C_1-C_{18} alkyne.

The C_1-C_{22} ether is defined by the following chemical structure:



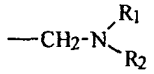
wherein R_4 + R_5 equals to C_2-C_{22}, and wherein R_4 is selected from the group consisting of straight or branched C_1-C_{18} alkyl, straight or branched C_1-C_{18} alkene, and C_1-C_{18} alkyne, and R_5 is selected from the group consisting of H, straight or branched C_1-C_{18} alkyl, straight or branched C_1-C_{18} alkene, and C_1-C_{18} alkyne.

Each R' is independently selected from the group consisting of H-, C_1-C_{22} alkyl, HO-CH_2, $CH_3CH(OH)$-, $HSCH_2$-, CH_3-SCH_2CH_2-, H_2NCOCH_2, $H_2NCOCH_2CH_2$-, $HOOCCH_2$-, $HOOCCH_2CH_2$-, and

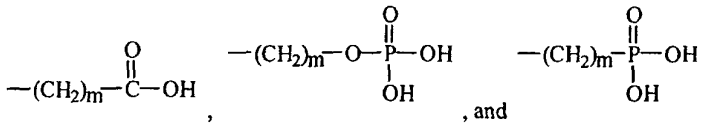


Each M is independently selected from the group consisting of H+, C_1-C_{22} alkyl, alkali metal ion, NH_4+, and aluminium ion.

"n" is an integer from 0 to 6.

Each R''' is independently selected from H or 

wherein R_1 and R_2 are independently selected from the group consisting of



wherein m is an integer from 1 to 3. These R''' chemical moieties increase the hydrophobic nature of the chelator, thereby increasing the ability of the entire chelator to penetrate into the superficial layers of the skin.

Preferred embodiments of the phenolic hydrophobic, metal ion chelators of the present invention are described below. These nonlimiting preferred embodiments also include methods of synthesizing each chelator, as well as the synthetic methods to obtain any commercially unavailable starting materials needed for the synthesis of the chelator.

A. Synthesis Part I: Phenolic Starting Material

The first synthetic step in the synthesis of the phenolic hydrophobic, metal ion chelators useful herein is the synthesis of the phenolic starting material having the following general chemical formula:

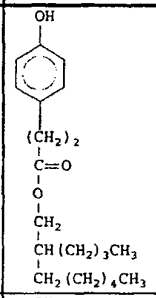
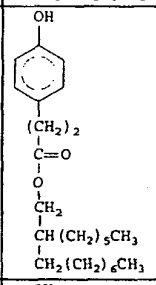
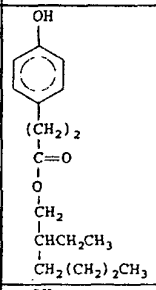
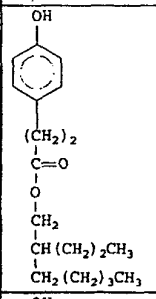
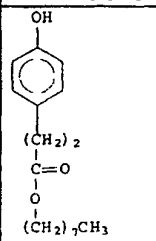
In one embodiment the phenolic starting material is nonylphenol (R is C_9H_{19}), which is obtained from the reaction of the propylene trimer. Nonylphenol is commercially available from Aldrich Chemical Co., Milwaukee, Wisconsin. In other embodiments, the phenolic starting material is not commercially available. In these embodiments, the phenolic starting material can be synthesized by reacting the appropriate carboxylic acid (e.g., dihydrocinnamic acid) with the appropriate alcohol (e.g., 2-butyl-octanol) in the presence of excess chlorotrimethylsilane, which serves to both catalyze the esterification reaction and to react with water, one of the by-products of the esterification reaction. The commercially unavailable phenolic starting materials, which are useful in the present invention, can be synthesized by following the synthetic protocol for preparing (2-Butyl-1-octyl)-4-hydroxybenzenepropanoate, as provided hereinafter.

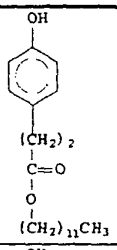
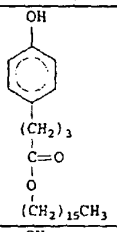
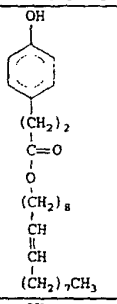
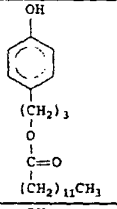
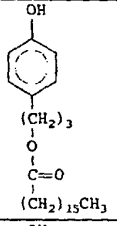
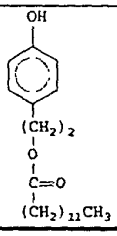
Preparation of (2-Butyl-1-octyl)-4-hydroxybenzenepropanoate: 4-Hydroxybenzenepropanoic acid (50 g, 0.3 mole) is placed in a 1 L round bottom flask equipped with a magnetic stirring bar and a

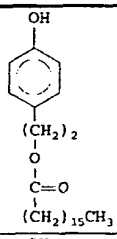
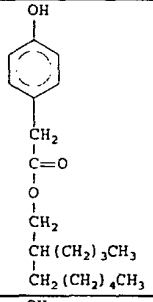
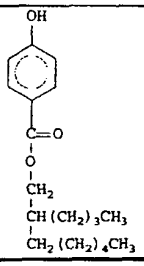
heating mantle. 2-Butyl-1-octanol (85 g, 0.46 mole) is then added in one portion and the mixture is warmed gently until most of the 4-hydroxybenzenepropanioc acid dissolves. After cooling slightly, tetrahydrofuran (50 mL) is added with stirring, thereby resulting in a homogeneous solution. Chlorotrimethylsilane (16 g, 0.15 mole) is then added in one portion, and the reaction mixture is again stirred at ambient temperature for 18 hrs. After adding ether (500 mL), the reaction mixture is added slowly to a rapidly stirred aqueous saturated sodium bicarbonate solution (500 mL). The quenched reaction mixture is then transferred to a separatory funnel, the layers are separated, and the organic layer is washed with a saturated sodium chloride solution (500 mL) and dried (Na_2SO_4). After removing the volatile components in vacuo using a rotary evaporator, the residue is heated under high vacuum (160 °C, 0.1 mm) to remove the unreacted 2-butyl-1-octanol. The resulting yellow oil (92.9 g, 92% yield) is then analyzed by ^1H and ^{13}C NMR: Spectra should be consistent with the structure of the desired phenolic starting material and should also indicate that the purity of the product is >92%. The product is also analyzed by CI MS: The presence of $M+NH_4^+$ at m/z 352 and $M+H^+$ at m/z 335 should be consistent with the molecular weight of the desired phenolic starting material.

The hereinbefore described methodology can be reapplied to synthesize a variety of phenolic starting groups. Nonlimiting examples of the phenolic starting materials and the chemical reaction materials needed for their synthesis are provide in the following table.

Table 1: Synthetic Reaction Materials Needed to Obtain Various Phenolic Starting Materials

Rxn	Carboxylic Acid Reactant	Alcohol Reactant	Reaction Product: Phenolic Starting Material	Yield	Chemical Structure
1	4-Hydroxy-benzenepropanoic acid	2-Butyl-1-octanol	(2-Butyl-1-octyl)-4-hydroxy-benzenepropanoate	92%	
2	4-Hydroxy-benzenepropanoic acid	2-Hexyl-1-decanol	(2-Hexyl-1-decyl)-4-hydroxy-benzenepropanoate	95%	
3	4-Hydroxy-benzen-propanoic acid	2-Ethyl-1-hexanol	(2-Ethyl-1-hexyl)-4-hydroxy-benzenepropanoate	75%	
4	4-Hydroxy-benzenepropanoic acid	2-Propyl-1-heptanol	(2-Propyl-1-heptyl)-4-hydroxy-benzenepropanoate	98%	
5	4-Hydroxy-benzenepropanoic acid	1-Octanol	1-Octyl-4-hydroxybenzene-propanoate	50%	

6	4-Hydroxy-benzenepropanoic acid	1-Dodecanol	1-Dodecyl-4-hydroxybenzene-propanoate	70%	
7	4-Hydroxy-benzenepropanoic acid	1-Hexadecanol	1-Hexadecyl-4-hydroxybenzene-propanoate	64%	
8	4-Hydroxy-benzenepropanoic acid	Oleyl alcohol	1-Oleyl-4-hydroxybenzene-propanoate	56%	
9	Lauric acid	3-(4-Hydroxy-phenyl)-1-propanol	3-(4-hydroxy-phenyl)propyl-dodecanoate	59%	
10	Palmitic acid	3-(4-Hydroxy-phenyl)-1-propanol	3-(4-hydroxy-phenyl)propyl-hexadecanoate	66%	
11	Lauric acid	4-Hydroxyphenyl-ethyl alcohol	2-(4-hydroxy-phenyl)ethyl-dodecanoate	37%	

12	Palmitic acid	4-Hydroxyphenyl-ethyl alcohol	2-(4-hydroxy-phenyl)ethyl-hexadecanoate	44%	
13	4-Hydroxyphenylacetic acid	2-Butyl-1-octanol	(2-Butyl-1-octyl)-4-hydroxyphenyl-acetate	94%	
14	4-Hydroxybenzoic acid	2-Butyl-1-octanol	(2-Butyl-1-octyl)-4-hydroxy-benzoate	51%	

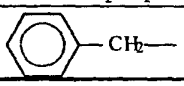
The phenolic starting materials described hereinbefore can then be used in the second step of the Mannich reaction described hereinafter. In the cases where the alkyl portion of the ester contains both straight chain and branched groups, each ester is prepared in pure form independently, then mixed prior to addition in the second synthetic step of the Mannich reaction. Of course, another way to accomplish this end result would be to mix the straight chain and branched alcohols before carrying out the esterification reaction. One could then use this mixture of esters directly for the second step of this Mannich reaction.

B. Synthesis Part II: Mannich Reaction to Obtain Oligomers

These phenolic hydrophobic, metal ion chelators of the defined structure described hereinbefore are prepared in a two-step reaction, which is generally referred to as a Mannich Reaction by those skilled in the art. In the first step, formaldehyde is reacted with an amino acid of the general formula $NH_2CHR'COOM$ in an aqueous solution whose pH is maintained at 7.5-8.0 with sodium or potassium hydroxide. A cosolvent, such as a C_1 to C_4 alcohol (e.g., methanol or isopropanol), is then added. In the second step while still maintaining the pH at 7.5-8.0, a methanol solution of a phenol starting material of the general formula

is slowly added to the reaction mixture, which is then heated at reflux. On cooling and standing, the desired product can be separated out as an oily layer while the water/methanol layer is decanted. To insure that the carboxylate groups are in their acid form, the product is refluxed with a large molar excess of acetic acid in toluene. The volatile components are removed under vacuum and the product is then dried and ground to a powder. Vacuum drying has been used for laboratory scale preparations, but other types of drying could obviously be employed for commercial purposes.

R', as hereinbefore described in the chemical structure for the chelators useful in the present invention, is the residue resulting form the α-amino acid. For example, if the amino acid used is glycine, R' = H; if alanine, R' = CH_3–, etc. The invention is not limited to cases where R' is a lower alkyl residue, but also includes residues consisting of hydroxyalkyl, thioalkyl, phenylalkyl, and other groups. By way of illustration, the following list contains various values of R' which are deemed to be within the scope of the present invention, as well as, the name of the amino acid from which that residue is obtained:

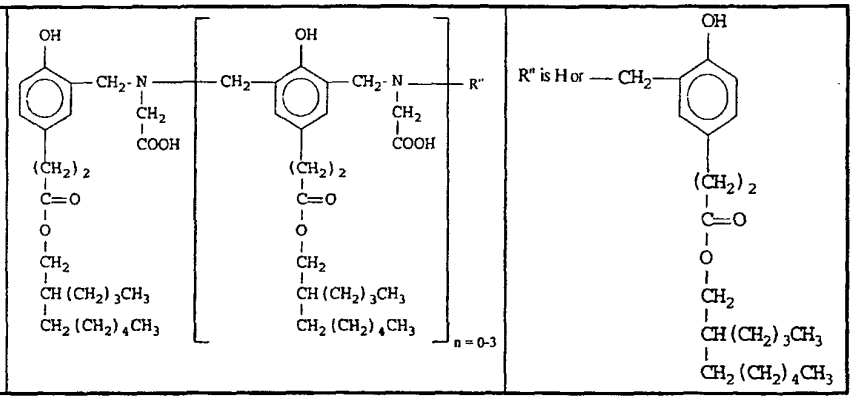
R' =	H–	glycine
	CH_3–	alanine
	CH_3CH_2–	α-amino bytyric acid
	$CH_3CH_2CH_2$–	iso-leucine acid
	$(CH_3)_2$–CH–	valine
	$(CH_3)_2$–$CHCH_2$–	leucine
	$CH_3CH_2CH(CH_3)$–	2-amino-3-methyl-pentanoic acid
	HO–CH_2–	serine
	$CH_3CH(OH)$–	threonine
	$HSCH_2$–	cysteine
	CH_3–S–CH_2CH_2–	methionine
	H_2NCOCH_2–	asparagine
	$H_2NCOCH_2CH_2$–	glutamine
	$HOOCCH_2$–	aspartic acid
	$HOOCCH_2CH_2$–	glutamic acid
		phenylalanine

The formaldehyde reactant may be supplied in any of its commercially available forms, such as formalin, paraformaldehyde, formcels, and trioxane.

Nonlimiting, preferred embodiments of the phenolic hydrophobic, metal ion chelators of the present invention are described hereinafter. These embodiments also provide specific descriptions to synthesize these embodiments.

(1) Oligomer 1 (Product of Mannich Rxn. with Phenolic Starting Material 1, R''' = H, and M = H): The phenolic hydrophobic, metal ion chelator of the following chemical structure described below can be obtained by following the synthetic steps described hereinafter.

Oligomer 1

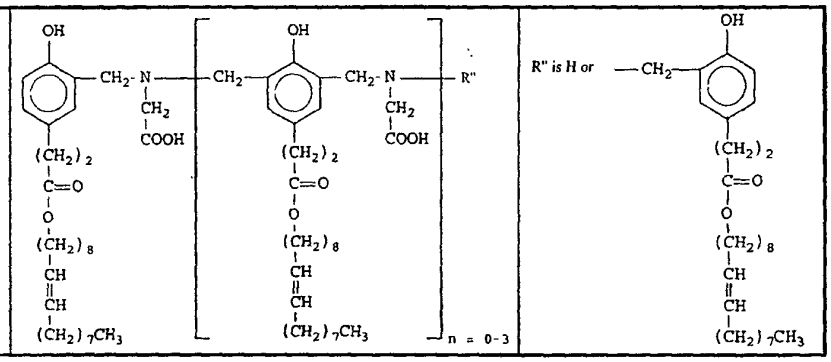


Glycine (14 g, 0.19 mole) is placed in a beaker equipped with a magnetic stirring bar and a pH electrode. Water (17 mL) and a 50% sodium hydroxide solution (7.6 g, 0.19 mole) is added with stirring. The mixture is adjusted to pH 8 using 1N hydrochloric acid (about 90 mL) at which point the glycine is dissolved thereby resulting in a homogeneous mixture. The solution is transferred to a 1 L 3-neck round bottom flask equipped with a reflux condenser, a thermometer, a pressure equalized addition funnel, and a heating mantel. Aqueous 37% formaldehyde solution (32 mL, 0.43 mole) is added dropwise over a period of 30 min, followed by the addition of 50% sodium hydroxide solution (7.6 g, 0.19 mole) and methanol (160 mL). The reaction mixture is then adjusted to pH 7.5 using 1 N sodium hydroxide (about 1 mL). The reaction mixture is then slowly heated to reflux while a solution of (2-butyl-1-octyl)-4-hydroxybenzenepropanoate (92.9 g, 0.28 mole) in methanol (100 mL) is added over a period of 2 hrs. Additional methanol (50 mL) is added and refluxing is continued for 16 hr. Upon cooling to ambient temperature, the reaction mixture should separate into two layers. The upper layer is then decanted from the viscous lower layer, and the lower layer is dissolved in ether (300 mL). This solution is dried (Na_2SO_4), concentrated in vacuo using a rotary evaporator, and the last traces of volatile materials are removed under high vacuum affording a viscous yellow oil. This oil is then extracted with acetonitrile (3 X 300 mL), which is effective for removing unreacted (2-butyl-1-octyl)-4-hydroxybenzenepropanoate. After dissolving the oil in toluene (300 mL), glacial acetic acid (105 mL) is added, and the solution is then refluxed for 30 min. The volatile components are removed in vacuo using a rotary evaporator. Hexane (500 mL) is then added to the residue and removed in vacuo several times to remove the entrapped acetic acid. The remaining volatiles are removed under high vacuum affording 87.1 g of light yellow semi-solid material. The semi-solid material is then analyzed by ^1H and ^{13}C NMR: Spectra should be consistent with a mixture of the desired oligomers. Analysis by reverse phase HPLC (Supelcosil LCAbz Plus column, MeOH/aqueous triethylammonium acetate buffer gradient mobile phase) and identification by

MS should confirm the presence of oligomers through n=3. Although quantitation can be difficult due to overlapping peaks, the oligomer distribution can be estimated to be about 3:2:1:0.5 for the n=0,1,2,3 oligomers, respectively.

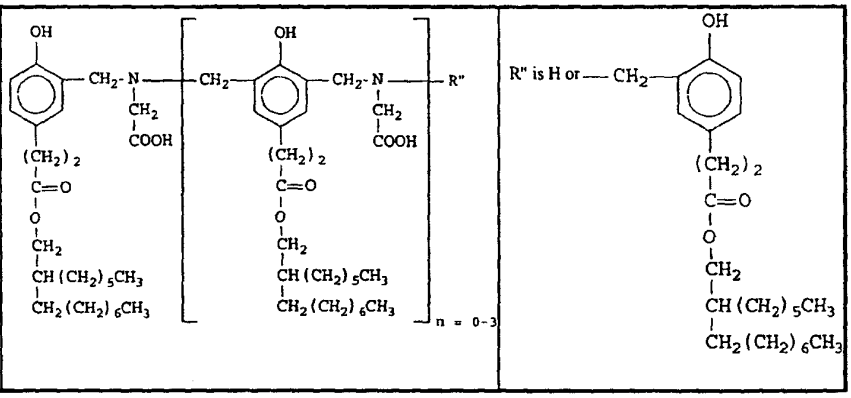
(2) Oligomer 2 (Product of Mannich Rxn. with Phenolic Starting Material 8, R''' = H, and M = H): The phenolic hydrophobic, metal ion chelator of the chemical structure described below can be obtained by following the synthetic steps described hereinbefore for Oligomer 1 except substituting the Phenolic Starting Material 1 with Phenolic Starting Material 8.

Oligomer 2



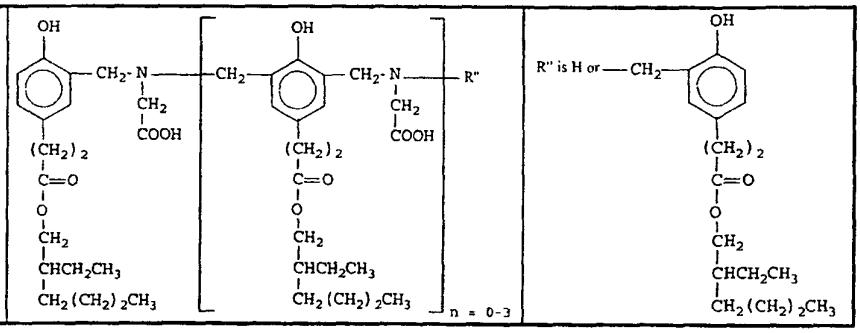
(3) Oligomer 3 (Product of Mannich Rxn. with Phenolic Starting Material 2, R''' = H, and M = H): The phenolic hydrophobic, metal ion chelator of the chemical structure described below can be obtained by following the synthetic steps described hereinbefore Oligomer 1 except substituting the Phenolic Starting Material 1 with Phenolic Starting Material 2.

Oligomer 3



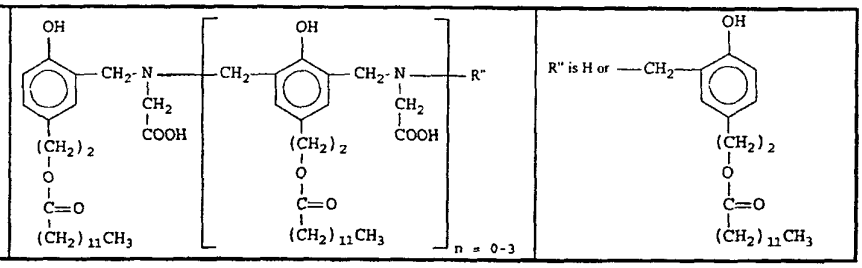
(4) Oligomer 4 (Product of Mannich Rxn. with Phenolic Starting Material 3, R''' = H, and M = H): The phenolic hydrophobic, metal ion chelator of the chemical structure described below can be obtained by following the synthetic steps described hereinbefore for Oligomer 1 except substituting the Phenolic Starting Material 1 with Phenolic Starting Material 3.

Oligomer 4



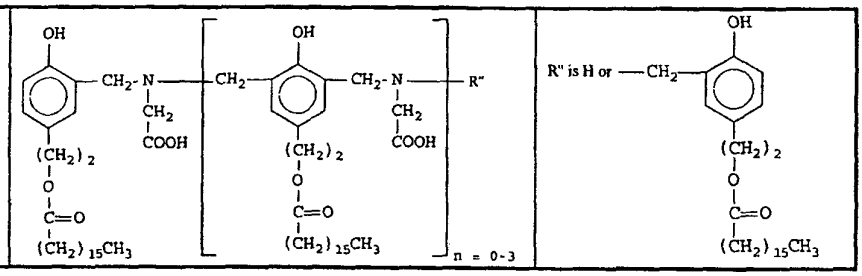
(5) Oligomer 5 (Product of Mannich Rxn. with Phenolic Starting Material 11, R''' = H, and M = H): The phenolic hydrophobic, metal ion chelator of the chemical structure described below can be obtained by following the synthetic steps described hereinbefore for Oligomer 1 except substituting the Phenolic Starting Material 1 with Phenolic Starting Material 11.

Oligomer 5



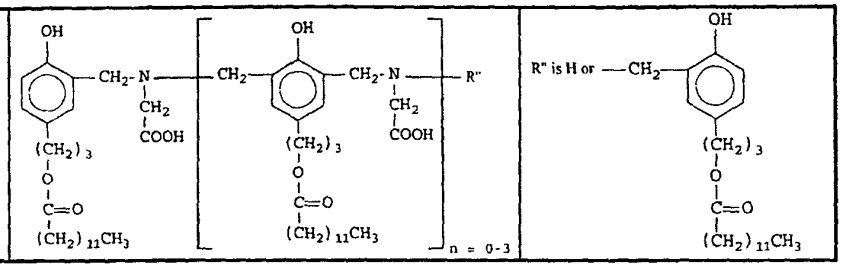
(6) Oligomer 6 (Product of Mannich Rxn. with Phenolic Starting Material 12, R''' = H, and M = H): The phenolic hydrophobic, metal ion chelator of the chemical structure described below can be obtained by following the synthetic steps described hereinbefore for Oligomer 1 except substituting the Phenolic Starting Material 1 with Phenolic Starting Material 12.

Oligomer 6



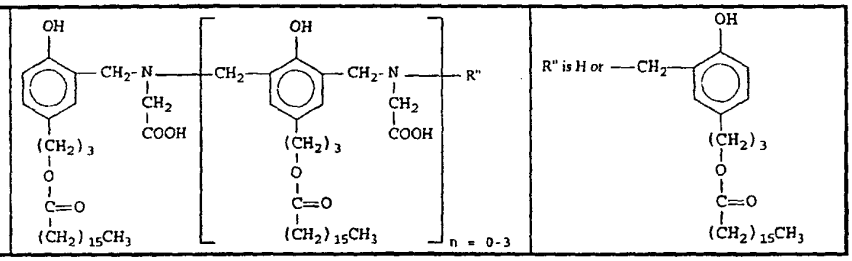
(7) Oligomer 7 (Product of Mannich Rxn. with Phenolic Starting Material 9, R''' = H, and M = H): The phenolic hydrophobic, metal ion chelator of the chemical structure described below can be obtained by following the synthetic steps described hereinbefore for Oligomer 1 except substituting the Phenolic Starting Material 1 with Phenolic Starting Material 9.

Oligomer 7



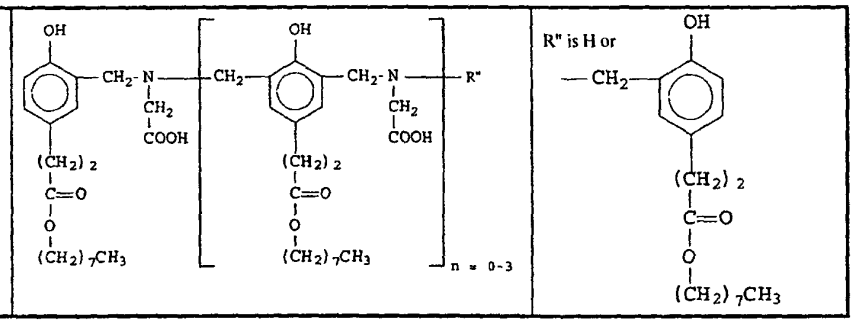
(8) Oligomer 8 (Product of Mannich Rxn. with Phenolic Starting Material 10, R''' = H, and M = H): The phenolic hydrophobic, metal ion chelator of the chemical structure described below can be obtained by following the synthetic steps described hereinbefore for Oligomer 1 except substituting the Phenolic Starting Material 1 with Phenolic Starting Material 10.

Oligomer 8



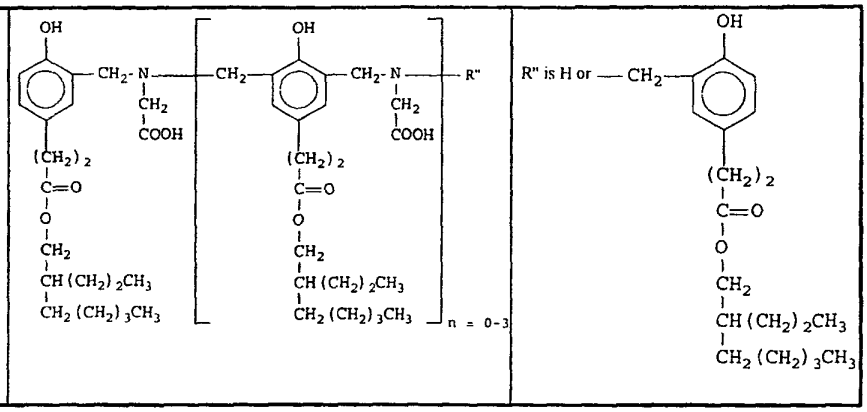
(9) Oligomer 9 (Product of Mannich Rxn. with Phenolic Starting Material 5, R''' = H, and M = H): The phenolic hydrophobic, metal ion chelator of the chemical structure described below can be obtained by following the synthetic steps described hereinbefore for Oligomer 1 except substituting the Phenolic Starting Material 1 with Phenolic Starting Material 5.

Oligomer 9



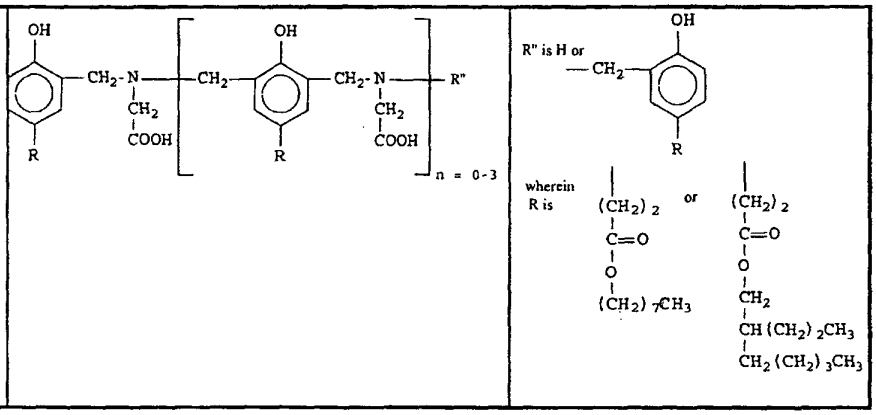
(10) Oligomer 10 (Product of Mannich Rxn. with Phenolic Starting Material 4, R''' = H, and M = H): The phenolic hydrophobic, metal ion chelator of the chemical structure described below can be obtained by following the synthetic steps described hereinbefore for Oligomer 1 except substituting the Phenolic Starting Material 1 with Phenolic Starting Material 4.

Oligomer 10



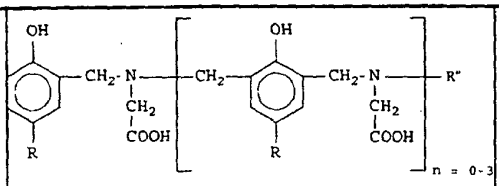
(11) Oligomer 11 (Product of Mannich Rxn. with 1:1 Mole Ratio of Phenolic Starting Materials 4 and 5, R''' = H, and M = H): The phenolic hydrophobic, metal ion chelator of the chemical structure described below can be obtained by following the synthetic steps described hereinbefore for Oligomer 1 except substituting the Phenolic Starting Material 1 with a 1:1 mole ratio of Phenolic Starting Materials 4 and 5.

Oligomer 11



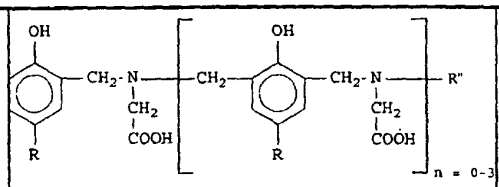
(12) Oligomer 12 (Product of Mannich Rxn. with 1:1 Mole Ratio of Phenolic Starting Materials 3 and 5, R''' = H, and M = H): The phenolic hydrophobic, metal ion chelator of the chemical structure described below can be obtained by following the synthetic steps described hereinbefore for Oligomer 1 except substituting the Phenolic Starting Material 1 with a 1:1 mole ratio of Phenolic Starting Materials 3 and 5.

Oligomer 12

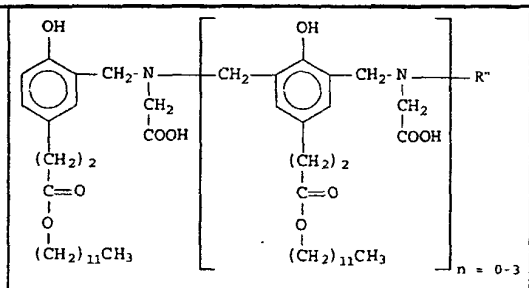
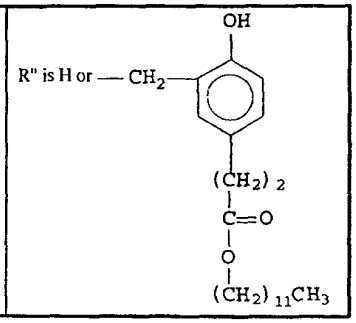


(13) Oligomer 13 (Product of Mannich Rxn. with 1:1 Mole Ratio of Phenolic Starting Materials 1 and 11, R''' = H, and M = H): The phenolic hydrophobic, metal ion chelator of the chemical structure described below can be obtained by following the synthetic steps described hereinbefore for Oligomer 1 except substituting the Phenolic Starting Material 1with a 1:1 mole ratio of Phenolic Starting Materials 1 and 11.

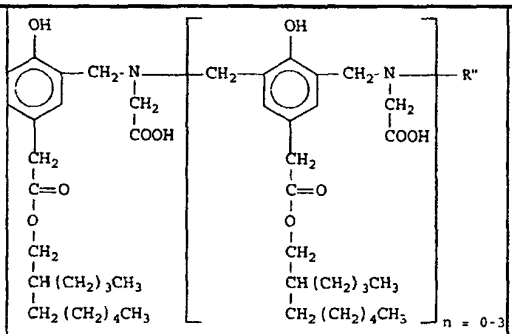
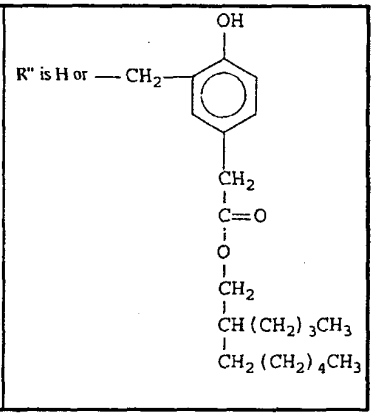
Oligomer 13



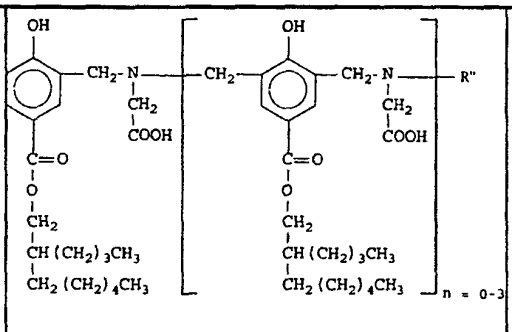
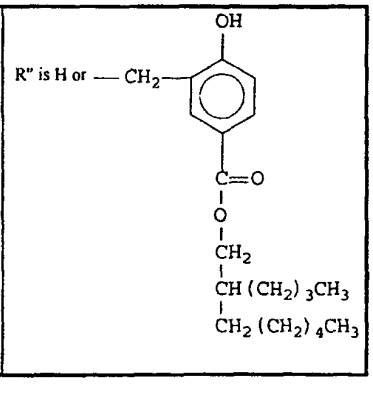
(14) Oligomer 14 (Product of Mannich Rxn. with Phenolic Starting Material 6, R''' = H, and M = H): The phenolic hydrophobic, metal ion chelator of the chemical structure described below can be obtained by following the synthetic steps described hereinbefore for Oligomer 1 except substituting the Phenolic Starting Material 1 with Phenolic Starting Material 6.

Oligomer 14		

(15) Oligomer 15 (Product of Mannich Rxn. with Phenolic Starting Material 13, R''' = H, and M = H): The phenolic hydrophobic, metal ion chelator of the chemical structure described below can be obtained by following the synthetic steps described hereinbefore for Oligomer 1 except substituting the Phenolic Starting Material 1 with Phenolic Starting Material 13.

Oligomer 15		

(16) Oligomer 16 (Product of Mannich Rxn. with Phenolic Starting Material 14, R''' = H, and M = H): The phenolic hydrophobic, metal ion chelator of the chemical structure described below can be obtained by following the synthetic steps described hereinbefore for Oligomer 1 except substituting the Phenolic Starting Material 1 with Phenolic Starting Material 14.

Oligomer 16		

(17) Skin Active Component Comprising Specific Oligomeric Content: The oligomeric content of the skin active component for one preferred embodiment of the present invention is such that a predominant portion of the skin active component comprises the skin care compound, hereinbefore described, having n values of ≥ 2. By "predominant portion," as used herein, is meant that this portion is present in the active component at a greater concentration than portions containing compounds having other discrete n values. A predominant portion of the skin active component in these embodiments of the present invention can contain a specific oligomeric content comprising greater than about 15%, preferably greater than about 17%, more preferably greater than about 20%, most preferably greater than about 22%, by weight of the skin active component, of a compound having n values of greater than 3.

The present inventors have surprisingly found these oligomers and skin active components containing predominant portions of these preferred oligomers to be especially useful in improving the appearance of dry skin.

Predominant portions of the skin active component containing compounds of specified n values described hereinbefore can be obtained by a variety of methods well known to those skilled in the art of organic chemistry. Generally, a skin active component containing specific oligomeric content can be obtained by two methods: (i) isolation/separation of the desired oligomers from the resulting chemical reaction product described hereinbefore in the "Phenolic Hydrophobic, Metal Ion Chelator" section and (ii) alter the chemical synthetic reaction to favor the formation of the desired oligomers.

Isolation Methods:

One approach to obtain compounds of specific n values is to isolate/separate the compounds of specified n values from the chemical mixture resulting from the synthetic reactions of the starting materials described hereinbefore. Various isolation techniques may be used and are well known to those skilled in the art. Such isolation/separation methods are described in Vogel, *Textbook of Practical Organic Chemistry* (5th Edition, revised by Furniss, B.S., Hannaford, A.B., Smith, P.W.G., and Tatchell, A.R., John Wiley & Sons) (1989), which reference is incorporated herein by reference in its entirety.

Fractionation: One method to isolate compounds of specific n values from the synthetic reaction mixtures such as the ones obtained in the present invention is by fractionation. One effective way to carry out such fractionations is by chromatography. Although there are many types of chromatographic procedures, flash chromatography is often very effective for preparative scale (large scale) fractionations. This technique is described in an article written by Still, Kahn, and Mitra, "Rapid Chromatographic Technique for Preparative Separations with Moderate Resolution", *Journal of Organic Chemistry*, Vol. 43, Page 2923 (1978), which reference is incorporated herein by reference in its entirety.

However, it is well known to one skilled in the art that compounds containing polar functional groups (e.g. carboxylic acids) are difficult to separate by chromatograph. Often, chromatographic resolution of such compounds may be improved by preparing a "derivative" which decreases the overall polarity of the compound. A suitable derivative is prepared by attaching a so-called "protective group" which can be removed easily after chromatographic fractionation is completed. The practice of using

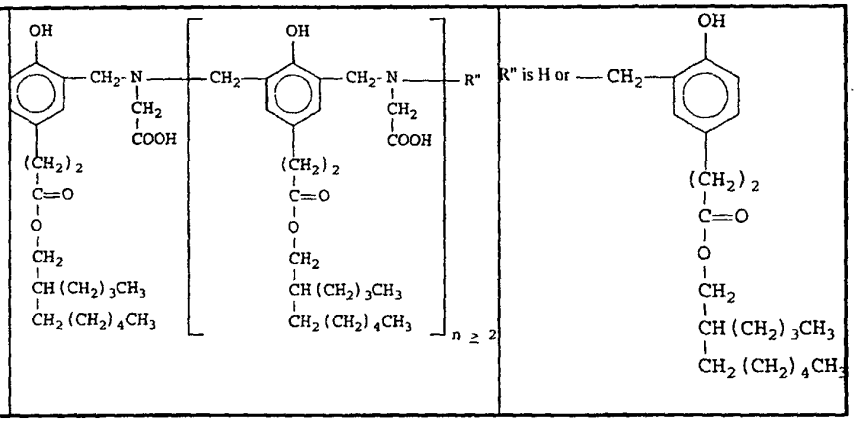
protective groups is described in detail in *Protective Groups in Organic Synthesis* written by T.W. Greene (Wiley Interscience 1981), which reference is incorporated herein by reference in its entirety. For fractionation of the chemical reaction product mixtures resulting from the synthetic reactions of the starting materials described hereinbefore to obtain the compounds of specified n values (e.g., $n \geq 2$), conversion of the carboxylic acids groups to benzyl esters by attaching the benzyl protective group is preferred because benzyl esters chromatograph with better resolution. In addition, the benzyl protective group is easily removed by hydrogenation.

Chemical Synthetic Reaction Methods

Another approach to obtain chemical reaction product mixtures containing predominant portions of a compound with specific n values is to alter the chemical reaction conditions. It is well known to one skilled in the art that temperature, pressure, concentration of reactants, and relative stoichiometry are typical reaction condition variables which effect oligomeric product distributions. A general description of the effects of these variables can be found in the book *Advanced Organic Chemistry, Reactions, Mechanisms, and Structure* written by J. March (3rd Ed., John Wiley & Sons, 1985), which reference is incorporated herein by reference in its entirety. For the Mannich reaction, the reaction used to prepare the compounds of some of the embodiments of the present invention, a more detailed description of the effects of these variables on product distributions can be found in two comprehensive review articles, which articles are incorporated herein by their entirety: M. Tramoutini, "Advances in the Chemistry of Mannich Bases," *Synthesis*, Pages 703 to 775 (1973), and M. Tramoutini and L. Angiolini, "Further Advances in the Chemistry of Mannich Bases", *Tetrahedron*, Volume 46, Pages 1791 to 1837 (1990).

For the specific oligomeric distribution of compounds of the present invention, a preferred method for increasing the fraction of the higher n value oligomers (e.g., larger n values, such as $n \geq 2$) involves carrying out the reaction at higher temperatures. Since this reaction involves the use of formaldehyde, which is a volatile ingredient, special measures are needed to carry out this reaction at temperatures above about 70 °C. A preferred method to maintain high concentrations of formaldehyde in solution at temperatures above about 70 °C is to increase the pressure of the phenolic hydrophobic, metal ion chelator reaction mixture, as described hereinbefore, using an inert gas, e.g., example nitrogen. The pressure should be high enough to keep most of the formaldehyde in solution at temperatures above about 70 °C (e.g., about 50-1500 psi). A high pressure autoclave is, therefore, recommended for such high temperature reactions.

A nonlimiting example for synthesizing one embodiment of a skin active component comprising n values of greater than or equal to 2 is provided hereinafter. Skin active components comprising phenolic hydrophobic, metal ion chelators of the chemical structure and oligomeric content described below can be obtained by following the synthetic steps described hereinafter.

Skin Active component comprising Oligomer 17	

Glycine (3.75 g, 0.05 mole) is placed in a beaker equipped with a magnetic stirring bar and a pH electrode. Water (9.2 mL) and a 50% sodium hydroxide solution (2.0 g, 0.025 mole) is added while stirring. The mixture is adjusted to pH 8 using 1N hydrochloric acid (about 25 mL) at which point the glycine dissolves thereby resulting in a homogeneous mixture. The solution is transferred to a 500 mL 3-neck round bottom flask equipped with a reflux condenser, a thermometer, a pressure equalized addition funnel, and a heating mantel. Aqueous 37% formaldehyde solution (8.4 mL, 0.11 mole) is then added dropwise over a period of 30 min, followed by the addition of 50% sodium hydroxide solution (2.0 g, 0.025 mole) and methanol (90 mL). The reaction mixture is adjusted to pH 7.5 using 1 N sodium hydroxide (about 1 mL). The reaction mixture is slowly heated to reflux while a solution of (2-butyl-1-octyl)-4-hydroxybenzenepropanoate (25 g, 0.075 mole) in methanol (40 mL) is added over a period of 0.5 hr. The reaction mixture is then transferred to a 2 L glass liner, placed in a Parr rocking autoclave, sealed, and pressurized to 1500 psig with nitrogen. The reaction mixture is rocked and heated at 120° C for 18 hr. After cooling, the autoclave is carefully depressurized and the brown, semi-solid reaction mixture is dissolved in ether (500 mL). This solution is then dried (Na_2SO_4), concentrated in vacuo using a rotary evaporator, and the last traces of volatile materials are removed under high vacuum affording a brown semi-solid product. This brown semi-solid product is extracted with acetonitrile (3 X 250 mL), which is effective for removing unreacted (2-butyl-1-octyl)-4-hydroxybenzenepropanoate. After the semi-solid residue from this extraction is dissolved in toluene (100 mL), glacial acetic acid (15 mL) is added and the solution is refluxed for 30 min. The volatile components are removed in vacuo using a rotary evaporator. Hexane (500 mL) is then added to the residue and removed in vacuo to aid in the removal of the entrapped acetic acid. This step is repeated several times until the odor of acetic acid in the residue is gone. The remaining volatiles are removed under high vacuum affording 11 g of brown semi-solid material. The product is then analyzed by ^1H and ^{13}C NMR: Spectra should be consistent with a mixture of the desired oligomers. Analysis by reverse phase HPLC (Supelcosil LCAbz Plus column, MeOH/aqueous triethylammonium acetate buffer gradient mobile phase) should indicate that the oligomer distribution had

clearly shifted to larger values of n. Quantitation is impossible due to broad, overlapping peaks, however the product is estimated to contain predominantly oligomers in which n=~3 to ~6.

Another method for increasing the fraction of the higher n value oligomers (e.g., larger n values, such as $n \geq 2$) involves increasing the time of the reaction.

A preferred method for increasing the fraction of lower n value oligomers (e.g., $n < 2$) involves carrying out the reaction at lower temperatures (e.g., 35 °C) and/or shortening the time of the reaction (e.g., less than about 90 minutes). Changing these reaction parameters (e.g., lowering the temperature or shortening the reaction time) can increase the fraction of the lower n value oligomers. However, a substantial portion of the larger n value oligomers will still be formed in the reaction product.

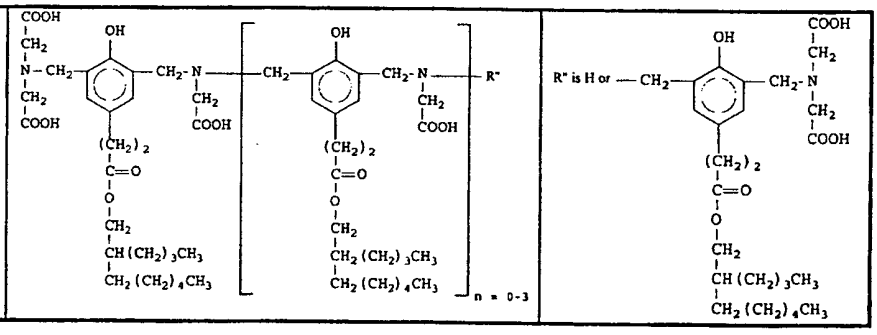
Changes in the oligomer distribution can also be brought about by changing the ratios of the reactions. However, this is less effective than the previously described methods.

C. Synthesis Part III: Adding Endcapped Chelating Moieties

The phenolic hydrophobic, metal ion chelators obtained form Synthesis Part II can be further modified to increase the metal ion chelating properties by endcapping these oligomers with chemical moieties which have metal ion chelating properties. Chemical moieties, which have a strong affinity to alkaline earth metal ions, include, but are not limited to, carboxylates, phosphates, phosphonates, phenols, amines, alcohols, ethers, and combinations thereof. The synthetic procedure, which can be applied to all of the chelators resulting from Synthesis Part II, is described hereinafter. In the synthetic protocol, methanol can be substituted with any appropriate C_1 to C_4 alcohol. However, methanol and isopropanol are preferred as solvents.

(1) Oligomer 18 (End-Capped Product of Oligomer 15): The phenolic hydrophobic, metal ion chelator of the following chemical structure described below can be obtained by following the synthetic steps described hereinafter.

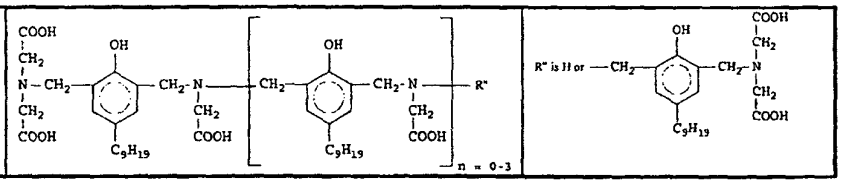
Oligomer 18



Iminodiacetic acid (6.66 g, 0.05 mole) is placed in a beaker equipped with a magnetic stirring bar and a pH electrode. Water (9.2 mL) and a 50% sodium hydroxide solution (2.0 g, 0.025 mole) are added while stirring. After adjusting the mixture to pH 8 using 1N hydrochloric acid, the solution is transferred to a 500 mL 3-neck round bottom flask equipped with a reflux condenser, a thermometer, a pressure

equalized addition funnel, and a heating mantel. Aqueous 37% formaldehyde solution (8.4 mL, 0.11 mole) is then added dropwise over a period of 5 min, followed by the addition of 50% sodium hydroxide solution (2.0 g, 0.025 mole), and methanol (90 mL). The reaction mixture is then adjusted to pH 7.5 using 1 N hydrochloric acid. The reaction mixture is then slowly heated to reflux while a solution of Oligomer 15 (16.5 g, about 0.2 mole) in isopropanol (75 mL) is added over a period of 1 hr. After the addition is complete the reaction mixture is allowed to reflux for 16 hrs. Upon cooling to ambient temperature, the reaction mixture separates into two layers. The upper layer is decanted from the viscous lower layer, and the lower layer is dissolved in ether (300 mL). This solution is then dried (Na_2SO_4), concentrated in vacuo using a rotary evaporator, and the last traces of volatile materials are removed under high vacuum affording a viscous yellow oil. This oil is extracted with acetonitrile (2 X 250 mL). The residue is then dissolved in toluene (75 mL), glacial acetic acid (9 mL) is added, and the solution is refluxed for 30 min. The volatile components are then removed in vacuo using a rotary evaporator. Hexane (100 mL) is added to the residue and removed in vacuo several times to remove the entrapped acetic acid. The remaining volatiles are removed under high vacuum affording about 8.28 g of dark yellow semi-solid material. The semi-solid material is then analyzed by ^1H and ^{13}C NMR: Spectra should be consistent with a mixture of the desired oligomers. Analysis by reverse phase HPLC (Supelcosil LCAbz Plus column, MeOH/aqueous triethylammonium acetate buffer gradient mobile phase) should indicate a similar distribution of oligomers with shorter retention times, which is consistent with the formation of the desired endcapped product.

(2) Oligomer 19 (End-Capped Product of the Mannich Reaction Using Nonylphenol): The phenolic hydrophobic, metal ion chelator of the chemical structure described below can be obtained by following the synthetic steps described hereinbefore for Oligomer 18 except substituting the Oligomer 15 with the product of the Mannich Reaction using nonylphenol.

Oligomer 19	

II. OPTIONAL DERMATOLOGICALLY ACCEPTABLE CARRIER

The phenolic hydrophobic, metal ion chelators of the present invention are preferably used in skin care compositions. Such skin care compositions can be obtained by formulated the chelators or skin care active components comprising the chelators into dermatologically acceptable carrier. Thus, such skin care compositions of the present invention can optionally comprise a dermatologically acceptable carrier. While a simple solution containing the skin active component is understood to be effective as a skin treating composition according to the present invention, compositions according to the invention can be in any appropriate forms for leave-on or rinse-off (either lathering or nonlather) topical application, e.g., solid, liquid, emulsion, gel, paste or mouse. The skin active component containing the hydrophobic, metal

ion chelators can also be applied to the skin in the neat form (e.g., without a dermatologically acceptable carrier). Thus, the compositions of the present invention comprise from 0.5% to about 99.9%, preferably from about 50% to about 99.8%, more preferably from about 75% to about 99.5%, and most preferably from about 90% to about 99%, by weight of the composition, of a dermatologically acceptable carrier.

The type of carrier utilized in the present invention depends on the type of product form desired for the composition. If the product form is a liquid or emulsion, however, it must utilize at least one liquid carrier or phase in which the skin active component may be soluble to at least about 0.1%, preferably about 0.2%, more preferable about 0.5%, and most preferably about 1%. Nonlimiting examples of product forms into which the skin active component of the present invention can be formulated include powders, soaps, cleansing cakes, lotions and creams, cleansing compositions, and foundations. Additional nonlimiting examples of product forms into which the skin active component can be formulated include aqueous solutions, anhydrous or oily gels, oil-in-water or water-in-oil emulsions (e.g., liquid, semi-liquid, solid, or semi-solid), dispersions of the ionic and/or nonionic type (e.g., containing microemulsions, or microcapsules, microparticles, or vesicles). Furthermore, the compositions as well as the skin active component of the present invention may be incorporated into various product forms generally utilized in the personal care area. Nonlimiting product forms which may incorporate the subject matter of the present invention include, but are not limited to, sanitizers (e.g., hand, full body, etc.), wipes or similar personal care implements (i.e., where the present compounds and compositions are applied onto or impregnated into the implement. In any event, the quantities of different constituents of the compositions according to the invention are those conventionally used in the fields considered. Some of these product forms are further described as follows.

Simple solutions of the skin active component are best achieved by using a solvent or mixture of solvents that falls within a specified solubility parameter range for the skin active component. A compilation of such values can be found in C. D. Vaughn, "Solubility Effects in Product, Package, Penetration, and Preservation," *Cosmetics & Toiletries*, Vol. 103, pages 47-69 (October, 1988). Those solvents (or systems) found to be most effective for solubilizing the skin active component have solubility parameters (or averages) in the range of about 7 to about 16. Nonlimiting examples of solvents are selected from the group consisting of water, ethanol, methanol, propyl alcohol, isopropyl alcohol, and mixtures thereof. When aqueous systems or aqueous phases are used as the carrier, the skin active component containing the phenolic hydrophobic, metal ion chelator is preferably complexed with an amine, more preferably a polyamine. This allows the phenolic hydrophobic, metal ion chelator to be water dispersible. Nonlimiting examples of polyamines useful herein are selected from the group consisting of polyethylene imine, polyvinylamine, polyallylamine, and mixtures thereof.

As noted, the topical compositions of the subject invention, including but not limited to lotions and creams, may comprise a hydrophobic component within the optional dermatologically acceptable carrier. Such compositions in this product form preferably contain from about 1% to about 50% of the hydrophobic component. A wide variety of suitable hydrophobic components are known and may be used

herein. Sagarin, *Cosmetics, Science and Technology*, 2nd Edition, Vol. 1, pp. 32-43 (1972), incorporated herein by reference, contains numerous examples of materials suitable as a hydrophobic component.

Lotions and creams according to the present invention generally comprise a solution carrier system and one or more hydrophobic components. Lotions typically comprise from about 1% to about 20%, preferably from about 2% to about 10%, of hydrophobic component; and from about 50% to about 90%, preferably from about 60% to about 80%, water. A cream typically comprises from about 2% to about 50%, preferably from about 3% to about 20%, of hydrophobic component; and from about 45% to about 85%, preferably from about 50% to about 75%, water.

Compositions of this invention useful for skin cleansing ("cleansers") are formulated with a suitable carrier, e.g., as described above, and preferably contain one or more dermatologically acceptable surfactants in an amount which is safe and effective for cleansing. Preferred compositions contain from about 1% to about 90%, more preferably from about 5% to about 10%, of a dermatologically acceptable surfactant. The surfactant is suitably selected from anionic, cationic, nonionic, zwitterionic, amphoteric and ampholytic surfactants, as well as mixtures of these surfactants. Such surfactants are well known to those skilled in the detergency art. Nonlimiting examples of possible surfactants include isoceteth-20, sodium methyl cocoyl taurate, sodium methyl oleoyl taurate, sodium lauryl sulfate, and betaines such as described herein. See U.S. Patent No. 4,800,197, to Kowcz et al., issued January 24, 1989, which is incorporated herein by reference in its entirety, for exemplary surfactants useful herein. Examples of a broad variety of additional surfactants useful herein are described in McCutcheon's Detergents and Emulsifiers, North American Edition (1986), published by Allured Publishing Corporation, which is incorporated herein by reference in its entirety. The skin cleansing compositions can optionally contain, at their art-established levels, other materials which are conventionally used in skin cleansing compositions.

The physical form of the cleansing compositions is not critical. The compositions can be, for example, formulated as liquids, shampoos, bath gels, pastes, or mousses. Preferred rinse-off cleansing compositions, such as shampoos, include a delivery system adequate to deposit sufficient levels of actives on the skin and scalp. A preferred delivery system involves the use of insoluble complexes. For a more complete disclosure of such delivery systems, see U.S. Patent 4,835,148, Barford et al., issued May 30, 1989, incorporated herein by reference in its entirety.

As used herein, the term "foundation" refers to a liquid, semi-liquid, or semi-solid skin cosmetic which includes, but is not limited to lotions, creams, gels, pastes, and the like. Typically the foundation is used over a large area of the skin, such as over the face, to provide a particular look. Foundations are typically used to provide an adherent base for color cosmetics such as rouge, blusher, and the like, and tend to hide skin imperfections and impart a smooth, even appearance to the skin. Foundations of the present invention include a dermatologically acceptable carrier for the essential particulate material and may include conventional ingredients such as oils, colorants, pigments, emollients, fragrances, waxes, stabilizers, and the like. Exemplary carriers and such other ingredients which are suitable for use herein are described, for example, in copending patent application Serial No. 08/430,961, filed on April 28, 1995

in the names of Marcia L. Canter, Brain D. Barford, and Brian D. Hofrichter, incorporated herein by reference.

A. Optional Carrier Ingredients

The dermatologically acceptable carrier of the present invention can also contain the usual adjuvants in the cosmetic and dermatological fields, such as hydrophilic and lipophilic gelling agents, hydrophilic and lipophilic active ingredients, preservatives, anti-oxidants, solvents, perfumes, sequestering agents, fillers, dyes or coloring agents, emulsifiers and surfactants. The quantities of these different adjuvants are those conventionally used in the fields considered, for example, 0.01-25 wt% of the total weight of the composition. Preferably, the compositions herein, and especially those in the form of emulsions, will also contain a hydrophobic component or phase that can contain a variety of hydrophobic materials.

1. Hydrophobic Components: Compositions according to the present invention, such as emulsions, can contain a hydrophobic phase comprising a lipid, oil, oily or other hydrophobic component. The compositions of the present invention preferably comprise from about 1% to about 98%, preferably from about 1% to about 50%, and more preferably from about 1% to about 30% by weight of the composition of a hydrophobic component. The hydrophobic component may be derived from animals, plants, or petroleum and may be natural or synthetic (i.e., man-made). Preferred hydrophobic components are substantially water-insoluble, more preferably essentially water-insoluble. Preferred hydrophobic components are those having a melting point of about 25°C or less under about one atmosphere of pressure.

A wide variety of suitable hydrophobic components are known and may be used herein and numerous examples can be found in Sagarin, Cosmetics, Science and Technology, 2nd Edition, Vol. 1, pp. 32-43 (1972), incorporated herein by reference. Nonlimiting examples of suitable hydrophobic components include those selected from the group consisting of:

(i) Mineral oil, which is also known as petrolatum liquid, is a mixture of liquid hydrocarbons obtained from petroleum. See The Merck Index, Tenth Edition, Entry 7048, p. 1033 (1983) and International Cosmetic Ingredient Dictionary, Fifth Edition, vol. 1, p.415-417 (1993), which are incorporated by reference herein in their entirety.

(ii) Petrolatum, which is also known as petroleum jelly, is a colloidal system of nonstraight-chain solid hydrocarbons and high-boiling liquid hydrocarbons, in which most of the liquid hydrocarbons are held inside the micelles. See The Merck Index, Tenth Edition, Entry 7047, p. 1033 (1983); Schindler, Drug. Cosmet. Ind., 89, 36-37, 76, 78-80, 82 (1961); and International Cosmetic Ingredient Dictionary, Fifth Edition, vol. 1, p. 537 (1993), which are incorporated by reference herein in their entirety.

(iii) Straight and branched chain hydrocarbons having from about 7 to about 40 carbon atoms. Nonlimiting examples of these hydrocarbon materials include dodecane, isododecane, squalane, cholesterol, hydrogenated polyisobutylene, docosane (i.e. a C_{22} hydrocarbon), hexadecane, isohexadecane

(a commercially available hydrocarbon sold as Permethyl® 101A by Presperse, South Plainfield, NJ). Also useful are the C7-C40 isoparaffins, which are C7-C40 branched hydrocarbons.

(iv) C1-C30 alcohol esters of C1-C30 carboxylic acids and of C2-C30 dicarboxylic acids, including straight and branched chain materials as well as aromatic derivatives (as used herein in reference to the hydrophobic component, mono- and poly- carboxylic acids include straight chain, branched chain and aryl carboxylic acids). Nonlimiting examples include diisopropyl sebacate, diisopropyl adipate, isopropyl myristate, isopropyl palmitate, methyl palmitate, myristyl propionate, 2-ethylhexyl palmitate, isodecyl neopentanoate, di-2-ethylhexyl maleate, cetyl palmitate, myristyl myristate, stearyl stearate, isopropyl stearate, methyl stearate, cetyl stearate, behenyl behenate, dioctyl maleate, dioctyl sebacate, diisopropyl adipate, cetyl octanoate, diisopropyl dilinoleate.

(v) Mono-, di- and tri- glycerides of C1-C30 carboxylic acids, e.g., caprylic/capric triglyceride, PEG-6 caprylic/capric triglyceride, PEG-8 caprylic/capric triglyceride.

(vi) Alkylene glycol esters of C1-C30 carboxylic acids, e.g., ethylene glycol mono- and di- esters, and propylene glycol mono- and di- esters of C1-C30 carboxylic acids e.g., ethylene glycol distearate.

(vii) Propoxylated and ethoxylated derivatives of the foregoing materials.

(viii) C1-C30 mono- and poly- esters of sugars and related materials. These esters are derived from a sugar or polyol moiety and one or more carboxylic acid moieties. Depending on the constituent acid and sugar, these esters can be in either liquid or solid form at room temperature. Examples of liquid esters include: glucose tetraoleate, the glucose tetraesters of soybean oil fatty acids (unsaturated), the mannose tetraesters of mixed soybean oil fatty acids, the galactose tetraesters of oleic acid, the arabinose tetraesters of linoleic acid, xylose tetralinoleate, galactose pentaoleate, sorbitol tetraoleate, the sorbitol hexaesters of unsaturated soybean oil fatty acids, xylitol pentaoleate, sucrose tetraoleate, sucrose pentaoletate, sucrose hexaoleate, sucrose hepatoleate, sucrose octaoleate, and mixtures thereof. Examples of solid esters include: sorbitol hexaester in which the carboxylic acid ester moieties are palmitoleate and arachidate in a 1:2 molar ratio; the octaester of raffinose in which the carboxylic acid ester moieties are linoleate and behenate in a 1:3 molar ratio; the heptaester of maltose wherein the esterifying carboxylic acid moieties are sunflower seed oil fatty acids and lignocerate in a 3:4 molar ratio; the octaester of sucrose wherein the esterifying carboxylic acid moieties are oleate and behenate in a 2:6 molar ratio; and the octaester of sucrose wherein the esterifying carboxylic acid moieties are laurate, linoleate and behenate in a 1:3:4 molar ratio. A preferred solid material is sucrose polyester in which the degree of esterification is 7-8, and in which the fatty acid moieties are C18 mono- and/or di-unsaturated and behenic, in a molar ratio of unsaturates:behenic of 1:7 to 3:5. A particularly preferred solid sugar polyester is the octaester of sucrose in which there are about 7 behenic fatty acid moieties and about 1 oleic acid moiety in the molecule. Other materials include cottonseed oil or soybean oil fatty acid esters of sucrose. The ester materials are further described in, U.S. Patent No. 2,831,854, U.S. Patent No. 4,005,196, to Jandacek, issued January 25, 1977; U.S. Patent No. 4,005,195, to Jandacek, issued January 25, 1977, U.S. Patent No.

5,306,516, to Letton et al., issued April 26, 1994; U.S. Patent No. 5,306,515, to Letton et al., issued April 26, 1994; U.S. Patent No. 5,305,514, to Letton et al., issued April 26, 1994; U.S. Patent No. 4,797,300, to Jandacek et al., issued January 10, 1989; U.S. Patent No. 3,963,699, to Rizzi et al, issued June 15, 1976; U.S. Patent No. 4,518,772, to Volpenhein, issued May 21, 1985; and U.S. Patent No. 4,517,360, to Volpenhein, issued May 21, 1985; all of which are incorporated by reference herein in their entirety.

(ix) Organopolysiloxane oils. The organopolysiloxane oil may be volatile, non-volatile, or a mixture of volatile and non-volatile silicones. The term "nonvolatile" as used in this context refers to those silicones that are liquid under ambient conditions and have a flash point (under one atmospheric of pressure) of or greater than about 100°C. The term "volatile" as used in this context refers to all other silicone oils. Suitable organopolysiloxanes can be selected from a wide variety of silicones spanning a broad range of volatilities and viscosities. Nonvolatile polysiloxanes are preferred. Nonlimiting examples of suitable silicones are disclosed in U.S. Patent No. 5,069,897, to Orr, issued December 3, 1991, which is incorporated by reference herein in its entirety. Examples of suitable organopolysiloxane oils include polyalkylsiloxanes, cyclic polyalkylsiloxanes, and polyalkylarylsiloxanes.

Polyalkylsiloxanes useful in the composition herein include polyalkylsiloxanes with viscosities of from about 0.5 to about 1,000,000 centistokes at 25°C. Such polyalkylsiloxanes can be represented by the general chemical formula $R_3SiO[R_2SiO]_xSiR_3$ wherein R is an alkyl group having from one to about 30 carbon atoms (preferably R is methyl or ethyl, more preferably methyl; also mixed alkyl groups can be used in the same molecule), and x is an integer from 0 to about 10,000, chosen to achieve the desired molecular weight which can range to over about 10,000,000. Commercially available polyalkylsiloxanes include the polydimethylsiloxanes, which are also known as dimethicones, examples of which include the Vicasil® series sold by General Electric Company and the Dow Corning® 200 series sold by Dow Corning Corporation. Specific examples of suitable polydimethylsiloxanes include Dow Corning® 200 fluid having a viscosity of 0.65 centistokes and a boiling point of 100°C, Dow Corning® 225 fluid having a viscosity of 10 centistokes and a boiling point greater than 200°C, and Dow Corning® 200 fluids having viscosities of 50, 350, and 12,500 centistokes, respectively, and boiling points greater than 200°C. Suitable dimethicones include those represented by the chemical formula $(CH_3)_3SiO[(CH_3)_2SiO]_x[CH_3RSiO]_ySi(CH_3)_3$ wherein R is straight or branched chain alkyl having from two to about 30 carbon atoms and x and y are each integers of 1 or greater selected to achieve the desired molecular weight which can range to over about 10,000,000. Examples of these alkyl-substituted dimethicones include cetyl dimethicone and lauryl dimethicone.

Cyclic polyalkylsiloxanes suitable for use in the composition include those represented by the chemical formula $[SiR_2\text{-}O]_n$ wherein R is an alkyl group (preferably R is methyl or ethyl, more preferably methyl) and n is an integer from about 3 to about 8, more preferably n is an integer from about 3 to about 7, and most preferably n is an integer from about 4 to about 6. When R is methyl, these materials are typically referred to as cyclomethicones. Commercially available cyclomethicones include Dow Corning

® 244 fluid having a viscosity of 2.5 centistokes, and a boiling point of 172°C, which primarily contains the cyclomethicone tetramer (i.e. n=4), Dow Corning® 344 fluid having a viscosity of 2.5 centistokes and a boiling point of 178°C, which primarily contains the cyclomethicone pentamer (i.e. n=5), Dow Corning ® 245 fluid having a viscosity of 4.2 centistokes and a boiling point of 205°C, which primarily contains a mixture of the cyclomethicone tetramer and pentamer (i.e. n=4 and 5), and Dow Corning® 345 fluid having a viscosity of 4.5 centistokes and a boiling point of 217°, which primarily contains a mixture of the cyclomethicone tetramer, pentamer, and hexamer (i.e. n=4, 5, and 6).

Also useful are materials such as trimethylsiloxysilicate, which is a polymeric material corresponding to the general chemical formula $[(CH_2)_3SiO_{1/2}]_x[SiO_2]y$, wherein x is an integer from about 1 to about 500 and y is an integer from about 1 to about 500. A commercially available trimethylsiloxysilicate is sold as a mixture with dimethicone as Dow Corning® 593 fluid.

Dimethiconols are also suitable for use in the composition. These compounds can be represented by the chemical formulas $R_3SiO[R_2SiO]_xSiR_2OH$ and $HOR_2SiO[R_2SiO]_xSiR_2OH$ wherein R is an alkyl group (preferably R is methyl or ethyl, more preferably methyl) and x is an integer from 0 to about 500, chosen to achieve the desired molecular weight. Commercially available dimethiconols are typically sold as mixtures with dimethicone or cyclomethicone (e.g. Dow Corning® 1401, 1402, and 1403 fluids).

Polyalkylaryl siloxanes are also suitable for use in the composition. Polymethylphenyl siloxanes having viscosities from about 15 to about 65 centistokes at 25°C are especially useful.

Preferred for use herein are organopolysiloxanes selected from the group consisting of polyalkylsiloxanes, alkyl substituted dimethicones, cyclomethicones, trimethylsiloxysilicates, dimethiconols, polyalkylaryl siloxanes, and mixtures thereof. More preferred for use herein are polyalkylsiloxanes and cyclomethicones. Preferred among the polyalkylsiloxanes are dimethicones.

(x) Vegetable oils and hydrogenated vegetable oils. Examples of vegetable oils and hydrogenated vegetable oils include safflower oil, castor oil, coconut oil, cottonseed oil, menhaden oil, palm kernel oil, palm oil, peanut oil, soybean oil, rapeseed oil, linseed oil, rice bran oil, pine oil, sesame oil, sunflower seed oil, hydrogenated safflower oil, hydrogenated castor oil, hydrogenated coconut oil, hydrogenated cottonseed oil, hydrogenated menhaden oil, hydrogenated palm kernel oil, hydrogenated palm oil, hydrogenated peanut oil, hydrogenated soybean oil, hydrogenated rapeseed oil, hydrogenated linseed oil, hydrogenated rice bran oil, hydrogenated sesame oil, hydrogenated sunflower seed oil, and mixtures thereof.

(xi) Animal fats and oils, e.g., lanolin and derivatives thereof, cod liver oil.

(xii) Other materials: Also useful are C4-C20 alkyl ethers of polypropylene glycols, C1-C20 carboxylic acid esters of polypropylene glycols, and di-C8-C30 alkyl ethers. Nonlimiting examples of these materials include PPG-14 butyl ether, PPG-15 stearyl ether, dioctyl ether, dodecyl octyl ether, and mixtures thereof.

2. Emulsion Compositions: Compositions of the present invention which contain hydrophobic components as hereinbefore described are frequently fashioned in the form of emulsions. Emulsions comprise a hydrophilic phase comprising a hydrophilic liquid or diluent, and a hydrophobic phase comprising a hydrophobic component, e.g., a lipid, oil or oily material. As well known to one skilled in the art, the hydrophilic phase will be dispersed in the hydrophobic phase, or vice versa, to form respectively hydrophilic or hydrophobic dispersed and continuous phases, depending on the composition ingredients. In emulsion technology, the term "dispersed phase" is a term well-known to one skilled in the art which means that the phase exists as small particles or droplets that are suspended in and surrounded by a continuous phase. The dispersed phase is also known as the internal or discontinuous phase. The emulsion may be or comprise (e.g., in a triple or other multi-phase emulsion) an oil-in-water emulsion or a water-in-oil emulsion such as a water-in-silicone emulsion. Oil-in-water emulsions typically comprise from about 1% to about 50% (preferably about 1% to about 30%) of the dispersed hydrophobic phase and from about 1% to about 98% (preferably from about 40% to about 90%) of the continuous hydrophilic phase; water-in-oil emulsions typically comprise from about 1% to about 98% (preferably from about 40% to about 90%) of the dispersed hydrophilic phase and from about 1% to about 50% (preferably about 1% to about 30%) of the continuous hydrophobic phase. The emulsion may also comprise a gel network, such as described in G. M. Eccleston, Application of Emulsion Stability Theories to Mobile and Semisolid O/W Emulsions, Cosmetics & Toiletries, Vol. 101, November 1996, pp. 73-92, incorporated herein by reference. Preferred emulsions are further described below.

Preferred emulsions have an apparent viscosity of from about 5,000 to about 200,000 centipoise (cps). For example, preferred lotions have an apparent viscosity of from about 10,000 to about 40,000 cps; preferred creams have an apparent viscosity of from about 60,000 to about 160,000 cps. Apparent viscosity can be determined using a Brookfield DVII RV viscometer, spindle TC, at 5 rpm, or the equivalent thereof. The viscosity is determined on the composition after the composition has been allowed to stabilize following its preparation, generally at least 24 hours under conditions of 25°C +/- 1°C and ambient pressure after preparation of the composition. Apparent viscosity is measured with the composition at a temperature of 25°C +/- 1°C, after 30 seconds spindle rotation.

The emulsion may contain an emulsifier and/or surfactant, generally to help disperse and suspend the discontinuous phase within the continuous phase. A wide variety of such agents can be employed. Known or conventional emulsifiers/surfactants can be used in the composition, provided that the selected agent is chemically and physically compatible with essential components of the composition, and provides the desired dispersion characteristics. Suitable agents include non-silicone-containing emulsifiers/surfactants, silicone emulsifiers/surfactants, and mixtures thereof.

In a preferred embodiment, the compositions herein comprise a hydrophilic emulsifier or surfactant. The compositions of the present invention preferably comprise from about 0.05% to about 5%, more preferably from about 0.05% to about 1% of at least one hydrophilic surfactant. Without intending

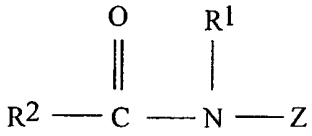
to be limited by theory, it is believed that the hydrophilic surfactant assists in dispersing hydrophobic materials, e.g., hydrophobic structuring agents, in the hydrophilic phase. The surfactant, at a minimum, must be hydrophilic enough to disperse in the hydrophilic phase. Preferred surfactants are those having an HLB of at least about 8. The exact surfactant chosen will depend upon the pH of the composition and the other components present.

Preferred hydrophilic surfactants are selected from nonionic surfactants. Among the nonionic surfactants that are useful herein are those that can be broadly defined as condensation products of long chain alcohols, e.g. C8-30 alcohols, with sugar or starch polymers, i.e., glycosides. These compounds can be represented by the formula $(S)_n$-O-R wherein S is a sugar moiety such as glucose, fructose, mannose, and galactose; n is an integer of from about 1 to about 1000, and R is a C8-30 alkyl group. Examples of long chain alcohols from which the alkyl group can be derived include decyl alcohol, cetyl alcohol, stearyl alcohol, lauryl alcohol, myristyl alcohol, oleyl alcohol, and the like. Preferred examples of these surfactants include those wherein S is a glucose moiety, R is a C8-20 alkyl group, and n is an integer of from about 1 to about 9. Commercially available examples of these surfactants include decyl polyglucoside (available as APG 325 CS from Henkel) and lauryl polyglucoside (available as APG 600 CS and 625 CS from Henkel).

Other useful nonionic surfactants include the condensation products of alkylene oxides with fatty acids (i.e. alkylene oxide esters of fatty acids). These materials have the general formula $RCO(X)_nOH$ wherein R is a C10-30 alkyl group, X is $-OCH_2CH_2-$ (i.e. derived from ethylene glycol or oxide) or $-OCH_2CHCH_3-$ (i.e. derived from propylene glycol or oxide), and n is an integer from about 6 to about 200. Other nonionic surfactants are the condensation products of alkylene oxides with 2 moles of fatty acids (i.e. alkylene oxide diesters of fatty acids). These materials have the general formula $RCO(X)_nOOCR$ wherein R is a C10-30 alkyl group, X is $-OCH_2CH_2-$(i.e. derived from ethylene glycol or oxide) or $-OCH_2CHCH_3-$(i.e. derived from propylene glycol or oxide), and n is an integer from about 6 to about 100. Other nonionic surfactants are the condensation products of alkylene oxides with fatty alcohols (i.e. alkylene oxide ethers of fatty alcohols). These materials have the general formula $R(X)_nOR'$ wherein R is a C10-30 alkyl group, X is $-OCH_2CH_2-$(i.e. derived from ethylene glycol or oxide) or $-OCH_2CHCH_3-$ (i.e. derived from propylene glycol or oxide), and n is an integer from about 6 to about 100 and R' is H or a C10-30 alkyl group. Still other nonionic surfactants are the condensation products of alkylene oxides with both fatty acids and fatty alcohols [i.e. wherein the polyalkylene oxide portion is esterified on one end with a fatty acid and etherified (i.e. connected via an ether linkage) on the other end with a fatty alcohol]. These materials have the general formula $RCO(X)_nOR'$ wherein R and R' are C10-30 alkyl groups, X is $-OCH_2CH_2$ (i.e. derived from ethylene glycol or oxide) or $-OCH_2CHCH_3-$ (derived from propylene glycol or oxide), and n is an integer from about 6 to about 100. Nonlimiting examples of these alkylene oxide derived nonionic surfactants include ceteth-6, ceteth-10, ceteth-12, ceteareth-6, ceteareth-10, ceteareth-12, steareth-6, steareth-10, steareth-12, steareth-21, PEG-6 stearate, PEG-10

stearate, PEG-100 stearate, PEG-12 stearate, PEG-20 glyceryl stearate, PEG-80 glyceryl tallowate, PEG-10 glyceryl stearate, PEG-30 glyceryl cocoate, PEG-80 glyceryl cocoate, PEG-200 glyceryl tallowate, PEG-8 dilaurate, PEG-10 distearate, and mixtures thereof.

Still other useful nonionic surfactants include polyhydroxy fatty acid amide surfactants corresponding to the structural formula:



wherein: R^1 is H, C_1-C_4 alkyl, 2-hydroxyethyl, 2-hydroxy- propyl, preferably C_1-C_4 alkyl, more preferably methyl or ethyl, most preferably methyl; R^2 is C_5-C_{31} alkyl or alkenyl, preferably C_7-C_{19} alkyl or alkenyl, more preferably C_9-C_{17} alkyl or alkenyl, most preferably C_{11}-C_{15} alkyl or alkenyl; and Z is a polhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with a least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably is a sugar moiety selected from the group consisting of glucose, fructose, maltose, lactose, galactose, mannose, xylose, and mixtures thereof. An especially preferred surfactant corresponding to the above structure is coconut alkyl N-methyl glucoside amide (i.e., wherein the R^2CO- moiety is derived from coconut oil fatty acids). Processes for making compositions containing polyhydroxy fatty acid amides are disclosed, for example, in G.B. Patent Specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd.; U.S. Patent No. 2,965,576, to E. R. Wilson, issued December 20, 1960; U.S. Patent No. 2,703,798, to A. M. Schwartz, issued March 8, 1955; and U.S. Patent No. 1,985,424, to Piggott, issued December 25, 1934; which are incorporated herein by reference in their entirety.

Preferred among the nonionic surfactants are those selected from the group consisting of steareth-21, ceteareth-20, ceteareth-12, sucrose cocoate, steareth-100, PEG-100 stearate, and mixtures thereof.

Other nonionic surfactants suitable for use herein include sugar esters and polyesters, alkoxylated sugar esters and polyesters, C1-C30 fatty acid esters of C1-C30 fatty alcohols, alkoxylated derivatives of C1-C30 fatty acid esters of C1-C30 fatty alcohols, alkoxylated ethers of C1-C30 fatty alcohols, polyglyceryl esters of C1-C30 fatty acids, C1-C30 esters of polyols, C1-C30 ethers of polyols, alkyl phosphates, polyoxyalkylene fatty ether phosphates, fatty acid amides, acyl lactylates, and mixtures thereof. Nonlimiting examples of these emulsifiers include: polyethylene glycol 20 sorbitan monolaurate (Polysorbate 20), polyethylene glycol 5 soya sterol, Steareth-20, Ceteareth-20, PPG-2 methyl glucose ether distearate, Ceteth-10, Polysorbate 80, cetyl phosphate, potassium cetyl phosphate, diethanolamine cetyl phosphate, Polysorbate 60, glyceryl stearate, polyoxyethylene 20 sorbitan trioleate (Polysorbate 85),

sorbitan monolaurate, polyoxyethylene 4 lauryl ether sodium stearate, polyglyceryl-4 isostearate, hexyl laurate, PPG-2 methyl glucose ether distearate, PEG-100 stearate, and mixtures thereof.

Another emulsifier useful herein are fatty acid ester blends based on a mixture of sorbitan or sorbitol fatty acid ester and sucrose fatty acid ester, the fatty acid in each instance being preferably C_8-C_{24}, more preferably C_{10}-C_{20}. The preferred fatty acid ester emulsifier is a blend of sorbitan or sorbitol C_{16}-C_{20} fatty acid ester with sucrose C_{10}-C_{16} fatty acid ester, especially sorbitan stearate and sucrose cocoate. This is commercially available from ICI under the trade name Arlatone 2121.

The hydrophilic surfactants useful herein can alternatively or additionally include any of a wide variety of cationic, anionic, zwitterionic, and amphoteric surfactants such as are known in the art. See, e.g., McCutcheon's, Detergents and Emulsifiers, North American Edition (1986), published by Allured Publishing Corporation; U.S. Patent No. 5,011,681 to Ciotti et al., issued April 30, 1991; U.S. Patent No. 4,421,769 to Dixon et al., issued December 20, 1983; and U.S. Patent No. 3,755,560 to Dickert et al., issued August 28, 1973; these four references are incorporated herein by reference in their entirety.

Exemplary cationic surfactants useful herein include those disclosed in U.S. Patent No. 5,151,209, to McCall et al., issued September 29, 1992; U.S. Patent No. 5,151,210, to Steuri et al., issued September 29, 1992; U.S. Patent No. 5,120,532, to Wells et al., issued June 9, 1992; U.S. Patent No. 4,387,090, to Bolich, issued June 7, 1983;; U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent No. 3,929,678, to Laughlin et al., issued December 30, 1975; U.S. Patent No. 3,959,461, to Bailey et al., issued May 25, 1976; McCutcheon's, Detergents & Emulsifiers, (North American edition 1979) M.C. Publishing Co.; and Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; all of these documents being incorporated herein by reference in their entirety. The cationic surfactants useful herein include cationic ammonium salts such as quaternary ammonium salts, and amino-amides.

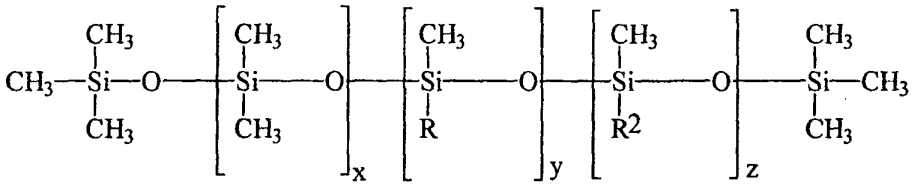
A wide variety of anionic surfactants are also useful herein. See, e.g., U.S. Patent No. 3,929,678, to Laughlin et al., issued December 30, 1975, which is incorporated herein by reference in its entirety. Nonlimiting examples of anionic surfactants include the alkoyl isethionates (e.g., C_{12} - C_{30}), alkyl and alkyl ether sulfates and salts thereof, alkyl and alkyl ether phosphates and salts thereof, alkyl methyl taurates (e.g., C_{12} - C_{30}), and soaps (e.g., alkali metal salts, e.g., sodium or potassium salts) of fatty acids.

Amphoteric and zwitterionic surfactants are also useful herein. Examples of amphoteric and zwitterionic surfactants which can be used in the compositions of the present invention are those which are broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 22 carbon atoms (preferably C_8 - C_{18}) and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples are alkyl imino acetates, and iminodialkanoates and aminoalkanoates, imidazolinium and ammonium derivatives. Other suitable

amphoteric and zwitterionic surfactants are those selected from the group consisting of betaines, sultaines, hydroxysultaines, alkyl sarcosinates (e.g., C_{12} - C_{30}), and alkanoyl sarcosinates.

Emulsions of the present invention can include a silicone containing emulsifier or surfactant. A wide variety of silicone emulsifiers are useful herein. These silicone emulsifiers are typically organically modified organopolysiloxanes, also known to those skilled in the art as silicone surfactants. Useful silicone emulsifiers include dimethicone copolyols. These materials are polydimethyl siloxanes which have been modified to include polyether side chains such as polyethylene oxide chains, polypropylene oxide chains, mixtures of these chains, and polyether chains containing moieties derived from both ethylene oxide and propylene oxide. Other examples include alkyl-modified dimethicone copolyols, i.e., compounds which contain C2-C30 pendant side chains. Still other useful dimethicone copolyols include materials having various cationic, anionic, amphoteric, and zwitterionic pendant moieties.

The dimethicone copolyol emulsifiers useful herein can be described by the following general structure:



wherein R is C1-C30 straight, branched, or cyclic alkyl and R^2 is selected from the group consisting of

$$--(CH_2)_n--O--(CH_2CHR^3O)_m--H,$$

and

$$--(CH_2)_n--O--(CH_2CHR^3O)_m--(CH_2CHR^4O)_o--H,$$

wherein n is an integer from 3 to about 10; R^3 and R^4 are selected from the group consisting of H and C1-C6 straight or branched chain alkyl such that R^3 and R^4 are not simultaneously the same; and m, o, x, and y are selected such that the molecule has an overall molecular weight from about 200 to about 10,000,000, with m, o, x, and y being independently selected from integers of zero or greater such that m and o are not both simultaneously zero, and z being independently selected from integers of 1 or greater. It is recognized that positional isomers of these copolyols can be achieved. The chemical representations depicted above for the R^2 moieties containing the R^3 and R^4 groups are not meant to be limiting but are shown as such for convenience.

Also useful herein, although not strictly classified as dimethicone copolyols, are silicone surfactants as depicted in the structures in the previous paragraph wherein R^2 is:

$$--(CH_2)_n--O--R^5,$$

wherein R^5 is a cationic, anionic, amphoteric, or zwitterionic moiety.

Nonlimiting examples of dimethicone copolyols and other silicone surfactants useful as emulsifiers herein include polydimethylsiloxane polyether copolymers with pendant polyethylene oxide sidechains, polydimethylsiloxane polyether copolymers with pendant polypropylene oxide sidechains,

polydimethylsiloxane polyether copolymers with pendant mixed polyethylene oxide and polypropylene oxide sidechains, polydimethylsiloxane polyether copolymers with pendant mixed poly(ethylene)(propylene)oxide sidechains, polydimethylsiloxane polyether copolymers with pendant organobetaine sidechains, polydimethylsiloxane polyether copolymers with pendant carboxylate sidechains, polydimethylsiloxane polyether copolymers with pendant quaternary ammonium sidechains; and also further modifications of the preceding copolymers containing pendant C2-C30 straight, branched, or cyclic alkyl moieties. Examples of commercially available dimethicone copolyols useful herein sold by Dow Corning Corporation are Dow Corning® 190, 193, Q2-5220, 2501 Wax, 2-5324 fluid, and 3225C (this later material being sold as a mixture with cyclomethicone). Cetyl dimethicone copolyol is commercially available as a mixture with polyglyceryl-4 isostearate (and) hexyl laurate and is sold under the tradename ABIL® WE-09 (available from Goldschmidt). Cetyl dimethicone copolyol is also commercially available as a mixture with hexyl laurate (and) polyglyceryl-3 oleate (and) cetyl dimethicone and is sold under the tradename ABIL® WS-08 (also available from Goldschmidt). Other nonlimiting examples of dimethicone copolyols also include lauryl dimethicone copolyol, dimethicone copolyol acetate, dimethicone copolyol adipate, dimethicone copolyolamine, dimethicone copolyol behenate, dimethicone copolyol butyl ether, dimethicone copolyol hydroxy stearate, dimethicone copolyol isostearate, dimethicone copolyol laurate, dimethicone copolyol methyl ether, dimethicone copolyol phosphate, and dimethicone copolyol stearate. See International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, which is incorporated by reference herein in its entirety.

Dimethicone copolyol emulsifiers useful herein are described, for example, in U.S. Patent No. 4,960,764, to Figueroa, Jr. et al., issued October 2, 1990; European Patent No. EP 330,369, to SaNogueira, published August 30, 1989; G. H. Dahms, et al., "New Formulation Possibilities Offered by Silicone Copolyols," Cosmetics & Toiletries, vol. 110, pp. 91-100, March 1995; M. E. Carlotti et al., "Optimization of W/O-S Emulsions And Study Of The Quantitative Relationships Between Ester Structure And Emulsion Properties," J. Dispersion Science And Technology, 13(3), 315-336 (1992); P. Hameyer, "Comparative Technological Investigations of Organic and Organosilicone Emulsifiers in Cosmetic Water-in-Oil Emulsion Preparations," HAPPI 28(4), pp. 88-128 (1991); J. Smid-Korbar et al., "Efficiency and usability of silicone surfactants in emulsions," Provisional Communication, International Journal of Cosmetic Science, 12, 135-139 (1990); and D. G. Krzysik et al., "A New Silicone Emulsifier For Water-in-Oil Systems," Drug and Cosmetic Industry, vol. 146(4) pp. 28-81 (April 1990); incorporated by reference herein in their entirety.

3. Polymeric Thickening Agent: The compositions of the present invention can also comprise a polymeric thickening agent. The polymeric thickening agent comprises from about 0.01% to about 10%, preferably from about 0.1% to about 5%, and more preferably from about 0.25% to about 2%, by weight of the composition. The polymeric thickening agent serves to increase the viscosity of the hydrophilic

liquid phase of the dermatologically carrier. In addition, the polymeric thickening agent also improves the aesthetics of the composition, e.g., good feel, nongreasiness, easy spreading, etc.

Nonlimiting types of preferred thickening agents suitable for use in the compositions herein include the following:

(i). Carboxylic Acid Polymers: These polymers are crosslinked compounds containing one or more monomers derived from acrylic acid, substituted acrylic acids, and salts and esters of these acrylic acids and the substituted acrylic acids, wherein the crosslinking agent contains two or more carbon-carbon double bonds and is derived from a polyhydric alcohol. The preferred carboxylic acid polymers are of two general types. The first type of polymer is a crosslinked homopolymer of an acrylic acid monomer or derivative thereof (e.g., wherein the acrylic acid has substituents on the two and three carbon positions independently selected from the group consisting of C_{1-4} alkyl, -CN, -COOH, and mixtures thereof). The second type of polymer is a crosslinked copolymer having a first monomer selected from the group consisting of an acrylic acid monomer or derivative thereof (as just described in the previous sentence), a short chain alcohol (i.e., a C_{1-4}) acrylate ester monomer or derivative thereof (e.g., wherein the acrylic acid portion of the ester has substituents on the two and three carbon positions independently selected from the group consisting of C_{1-4} alkyl, -CN, -COOH, and mixtures thereof), and mixtures thereof; and a second monomer which is a long chain alcohol (i.e. C_{8-40}) acrylate ester monomer or derivative thereof (e.g., wherein the acrylic acid portion of the ester has substituents on the two and three carbon positions independently selected from the group consisting of C_{1-4} alkyl, -CN, -COOH, and mixtures thereof). Combinations of these two types of polymers are also useful herein.

In the first type of crosslinked homopolymers, the monomers are preferably selected from the group consisting of acrylic acid, methacrylic acid, ethacrylic acid, and mixtures thereof, with acrylic acid being most preferred. In the second type of crosslinked copolymers the acrylic acid monomer or derivative thereof is preferably selected from the group consisting of acrylic acid, methacrylic acid, ethacrylic acid, and mixtures thereof, with acrylic acid, methacrylic acid, and mixtures thereof being most preferred. The short chain alcohol acrylate ester monomer or derivative thereof is preferably selected from the group consisting of C_{1-4} alcohol acrylate esters, C_{1-4} alcohol methacrylate esters, C_{1-4} alcohol ethacrylate esters, and mixtures thereof, with the C_{1-4} alcohol acrylate esters, C_{1-4} alcohol methacrylate esters, and mixtures thereof, being most preferred. The long chain alcohol acrylate ester monomer is selected from C_{8-40} alkyl acrylate esters, with C_{10-30} alkyl acrylate esters being preferred.

The crosslinking agent in both of these types of polymers is a polyalkenyl polyether of a polyhydric alcohol containing more than one alkenyl ether group per molecule, wherein the parent polyhydric alcohol contains at least 3 carbon atoms and at least 3 hydroxyl groups. Preferred crosslinkers are those selected from the group consisting of allyl ethers of sucrose and allyl ethers of pentaerythritol, and mixtures thereof. These polymers useful in the present invention are more fully described in U.S. Patent No. 5,087,445, to Haffey et al., issued February 11, 1992; U.S. Patent No. 4,509,949, to Huang et

al., issued April 5, 1985; U.S. Patent No. 2,798,053, to Brown, issued July 2, 1957; which are both incorporated by reference herein in their entirety. See also, CTFA International Cosmetic Ingredient Dictionary, fourth edition, 1991, pp. 12 and 80; which are also incorporated herein by reference in their entirety.

Examples of commercially available homopolymers of the first type useful herein include the carbomers, which are homopolymers of acrylic acid crosslinked with allyl ethers of sucrose or pentaerytritol. The carbomers are available as the Carbopol® 900 series from B.F. Goodrich (e.g., Carbopol® 954). Examples of commercially available copolymers of the second type useful herein include copolymers of C_{10-30} alkyl acrylates with one or more monomers of acrylic acid, methacrylic acid, or one of their short chain (i.e. C_{1-4} alcohol) esters, wherein the crosslinking agent is an allyl ether of sucrose or pentaerytritol. These copolymers are known as acrylates/C10-30 alkyl acrylate crosspolymers and are commercially available as Carbopol® 1342, Carbopol® 1382Pemulen TR-1, and Pemulen TR-2, from B.F. Goodrich. In other words, examples of carboxylic acid polymer thickeners useful herein are those selected from the group consisting of carbomers, acrylates/C10-C30 alkyl acrylate crosspolymers, and mixtures thereof.

(ii). Crosslinked Polyacrylate Polymers

The crosslinked polyacrylate polymers useful as thickeners or gelling agents include both cationic and nonionic polymers, with the cationics being generally preferred. Examples of useful crosslinked nonionic polyacrylate polymers and crosslinked cationic polyacrylate polymers are those described in U.S. Patent 5,100,660, to Hawe et al., issued March 31, 1992; U.S. Patent 4,849,484, to Heard, issued July 18, 1989; U.S. Patent 4,835,206, to Farrar et al., issued May 30, 1989; U.S. Patent 4,628,078 to Glover et al. issued December 9, 1986; U.S. Patent 4,599,379 to Flesher et al. issued July 8, 1986; and EP 228,868, to Farrar et al., published July 15, 1987; all of which are incorporated by reference herein in their entirety.

The crosslinked polyacrylate polymers are high molecular weight materials that can be characterized by the general formula: $(A)_l(B)_m(C)_n$ and comprise the monomer units $(A)_l$, $(B)_m$, and $(C)_n$, wherein (A) is a dialkylaminoalkyl acrylate monomer or its quaternary ammonium or acid addition salt, (B) is a dialkylaminoalkyl methacrylate monomer or its quaternary ammonium or acid addition salt, (C) is a monomer that is polymerizable with (A) or (B), for example a monomer having a carbon-carbon double bond or other such polymerizable functional group, l is an integer of 0 or greater, m is an integer of 0 or greater, n is an integer of 0 or greater, but where either l or m, or both, must be 1 or greater.

The (C) monomer can be selected from any of the commonly used monomers. Nonlimiting examples of these monomers include ethylene, propylene, butylene, isobutylene, eicosene, maleic anhydride, acrylamide, methacrylamide, maleic acid, acrolein, cyclohexene, ethyl vinyl ether, and methyl vinyl ether. In the cationic polymers of the present invention, (C) is preferably acrylamide. The alkyl portions of the (A) and (B) monomers are short chain length alkyls such as C_1-C_8, preferably C_1-C_5, more preferably C_1-C_3, and most preferably C_1-C_2. When quaternized, the polymers are preferably quaternized with short chain alkyls, i.e., C_1-C_8, preferably C_1-C_5, more preferably C_1-C_3, and most preferably C_1-C_2. The acid addition salts refer to polymers having protonated amino groups. Acid addition salts can be performed through the use of halogen (e.g. chloride), acetic, phosphoric, nitric, citric, or other acids.

These $(A)_l(B)_m(C)_n$ polymers also comprise a crosslinking agent, which is most typically a material containing two or more unsaturated functional groups. The crosslinking agent is reacted with the monomer units of the polymer and is incorporated into the polymer thereby forming links or covalent bonds between two or more individual polymer chains or between two or more sections of the same polymer chain. Nonlimiting examples of suitable crosslinking agents include those selected from the group consisting of methylenebisacrylamides, diallyldialkyl ammonium halides, polyalkenyl polyethers of polyhydric alcohols, allyl acrylates, vinyloxyalkylacrylates, and polyfunctional vinylidenes. Specific examples of crosslinking agents useful herein include those selected from the group consisting of methylenebisacrylamide, ethylene glycol di-(meth)acrylate, di-(meth)acrylamide, cyanomethylacrylate, vinyloxyethylacrylate, vinyloxyethylmethacrylate, allyl pentaerythritol, trimethylolpropane diallylether, allyl sucrose, butadiene, isoprene, divinyl benzene, divinyl naphthalene, ethyl vinyl ether, methyl vinyl

ether, and allyl acrylate. Other crosslinkers include formaldehyde and glyoxal. Preferred for use herein as a crosslinking agent is methylenebisacrylamide.

Widely varying amounts of the crosslinking agent can be employed depending upon the properties desired in the final polymer, e.g. viscosifying effect. Without being limited by theory, it is believed that incorporation of a crosslinking agent into these cationic polymers provides a material that is a more effective viscosifying agent without negatives such as stringiness and viscosity breakdown in the presence of electrolytes. The crosslinking agent, when present, can comprise from about 1 ppm to about 1000 ppm, preferably from about 5 ppm to about 750 ppm, more preferably from about 25 ppm to about 500 ppm, even more preferably from about 100 ppm to about 500 ppm, and most preferably from about 250 ppm to about 500 ppm of the total weight of the polymer on a weight/weight basis.

The intrinsic viscosity of the crosslinked polymer, measured in one molar sodium chloride solution at 25 °C, is generally above 6, preferably from about 8 to about 14. The molecular weight (weight average) of the crosslinked polymers hereof is high, and is believed to typically be between about 1 million and about 30 million. The specific molecular weight is not critical and lower or higher weight average molecular weights can be used as long as the polymer retains its intended viscosifying effects. Preferably, a 1.0% solution of the polymer (on an actives basis) in deionized water will have a viscosity at 25°C of at least about 20,000 cP, preferably at least about 30,000 cP, when measured at 20 RPM by a Brookfield RVT (Brookfield Engineering Laboratories, Inc. Stoughton, MA, USA).

These cationic polymers can be made by polymerization of an aqueous solution containing from about 20% to about 60%, generally from about 25% to about 40%, by weight monomer, in the presence of an initiator (usually redox or thermal) until the polymerization terminates. The crosslinking agent can also be added to the solution of the monomers to be polymerized, to incorporate it into the polymer. In the polymerization reactions, the temperature generally starts between about 0° and 95°C. The polymerization can be conducted by forming a reverse phase dispersion of an aqueous phase of the monomers (and also any additional crosslinking agents) into a nonaqueous liquid, e.g. mineral oil, lanolin, isododecane, oleyl alcohol, and other volatile and nonvolatile esters, ethers, and alcohols, and the like.

All percentages describing the polymer in this section of the description herein are molar, unless otherwise specified. When the polymer contains (C) monomer, the molar proportion of (C) monomer, based on the total molar amount of (A), (B), and (C), can be from 0% to about 99%. The molar proportions of (A) and (B) can each be from 0% to 100%. When acrylamide, is used as the (C) monomer, it will preferably be used at a level of from about 20% to about 99%, more preferably from about 50% to about 90%.

Where monomer (A) and (B) are both present, the ratio of monomer (A) to monomer (B) in the final polymer, on a molar basis, is preferably from about 99:5 to about 15:85, more preferably from about 80:20 to about 20:80. Alternatively, in another class of polymers, the ratio is from about 5:95 to about 50:50, preferably from about 5:95 to about 25:75.

In another alternative class of polymers, the ratio (A):(B) is from about 50:50 to about 85:15. Preferably the ratio (A):(B) is about 60:40 to about 85:15, most preferably about 75:25 to about 85:15.

Most preferred is where monomer (A) is not present and the ratio of monomer (B):monomer (C) is from about 30:70 to about 70:30, preferably from about 40:60 to about 60:40 and most preferably from about 45:55 to about 55:45.

Cationic polymers that are useful herein that are especially preferred are those conforming to the general structure $(A)_l(B)_m(C)_n$ wherein l is zero, (B) is methyl quaternized dimethylaminoethyl methacrylate, the ratio of (B):(C) is from about 45:55 to about 55:45, and the crosslinking agent is methylenebisacrylamide. An example of such a cationic polymer is one that is commercially available as a mineral oil dispersion (which can also include various dispersing aids such as PPG-1 trideceth-6) under the trademark Salcare® SC92 from Allied Colloids Ltd. (Norfolk, Virginia). This polymer has the proposed CTFA designation, "Polyquaternium 32 (and) Mineral Oil".

Other cationic polymers useful herein, are those not containing acrylamide or other (C) monomers, that is, n is zero. In these polymers the (A) and (B) monomer components are as described above. An especially preferred group of these non-acrylamide containing polymers is one in which l is also zero. In this instance the polymer is essentially a homopolymer of a dialkylaminoalkyl methacrlyate monomer or its quaternary ammonium or acid addition salt. These diaklylaminoalkyl methacrylate polymers preferably contain a crosslinking agent as described above.

A cationic polymer, which is essentially a homopolymer, useful herein is one conforming to the general structure $(A)_l(B)_m(C)_n$ wherein l is zero, (B) is methyl quaternized dimethylaminoethyl methacrylate, n is zero, and the crosslinking agent is methylenebisacrylamide. An example of such a homopolymer is commercially available as a mixture containing approximately 50% of the polymer, approximately 44% mineral oil, and approximately 6% PPG-1 trideceth-6 as a dispersing aid, from Allied Colloids Ltd, (Norfolk, VA) under the trademark Salcare® SC95. This polymer has recently been given the CTFA designation "Polyquaternium 37 (and) Mineral Oil (and) PPG-1 Trideceth-6".

(iii). Polyacrylamide Polymers: Also useful herein as thickening agents are polyacrylamide polymers, especially non-ionic polyacrylamide polymers including substituted branched or unbranched polymers. These polymers can be formed from a variety of monomers including acrylamide and methacrylamide which are unsubstituted or substituted with one or two alkyl groups (preferably C_1 to C_5). Preferred are acrylate amide and methacrylate amide monomers in which the amide nitrogen is unsubstituted, or substituted with one or two C_1 to C_5 alkyl groups (preferably methyl, ethyl, or propyl), for example, acrylamide, methacrylamide, N-methacrylamide, N-methylmethacrylamide, N,N-dimethylmethacrylamide, N-isopropylacrylamide, N-isopropylmethacrylamide, and N,N-dimethylacrylamide. These polymers have a molecular weight greater than about 1,000,000 preferably greater than about 1,5000,000 and range up to about 30,000,000. Most preferred among these polyacrylamide polymers is the non-ionic polymer given the CTFA designation polyacrylamide and

isoparaffin and laureth-7, available under the Tradename Sepigel 305 from Seppic Corporation (Fairfield, NJ).

Other polyacrylamide polymers useful herein include multi-block copolymers of acrylamides and substituted acrylamides with acrylic acids and substituted acrylic acids. Commercially available examples of these multi-block copolymers include Hypan SR150H, SS500V, SS500W, SSSA100H, from Lipo Chemicals, Inc., (Patterson, NJ).

(iv). Polysaccharides: A wide variety of polysaccharides are useful herein as thickening agents. By "polysaccharides" are meant gelling agents containing a backbone of repeating sugar (i.e. carbohydrate) units. Nonlimiting examples of polysaccharide gelling agents include those selected from the group consisting of cellulose, carboxymethyl hydroxyethylcellulose, cellulose acetate propionate carboxylate, hydroxyethylcellulose, hydroxyethyl ethylcellulose, hydroxypropylcellulose, hydroxypropyl methylcellulose, methyl hydroxyethylcellulose, microcrystalline cellulose, sodium cellulose sulfate, and mixtures thereof. Also useful herein are the alkyl substituted celluloses. In these polymers, the hydroxy groups of the cellulose polymer is hydroxyalkylated (preferably hydroxyethylated or hydroxypropylated) to form a hydroxyalkylated cellulose which is then further modified with a C10-C30 straight chain or branched chain alkyl group through an ether linkage. Typically these polymers are ethers of C10-C30 straight or branched chain alcohols with hydroxyalkylcelluloses. Examples of alkyl groups useful herein include those selected from the group consisting of stearyl, isostearyl, lauryl, myristyl, cetyl, isocetyl, cocoyl (i.e. alkyl groups derived from the alcohols of coconut oil), palmityl, oleyl, linoleyl, linolenyl, ricinoleyl, behenyl, and mixtures thereof. Preferred among the alkyl hydroxyalkyl cellulose ethers is the material given the CTFA designation cetyl hydroxyethylcellulose, which is the ether of cetyl alcohol and hydroxyethylcellulose. This material is sold under the tradename Natrosol® CS Plus from Aqualon Corporation.

Other useful polysaccharides include scleroglucans comprising a linear chain of (1->3) linked glucose units with a (1->6) linked glucose every three units, a commercially available example of which is Clearogel™ CS11 from Michel Mercier Products Inc. (Mountainside, NJ).

(iv). Gums: Other additional thickening and gelling agents useful herein include materials which are primarily derived from natural sources. Nonlimiting examples of these gelling agent gums include materials selected from the group consisting of acacia, agar, algin, alginic acid, ammonium alginate, amylopectin, calcium alginate, calcium carrageenan, carnitine, carrageenan, dextrin, gelatin, gellan gum, guar gum, guar hydroxypropyltrimonium chloride, hectorite, hyaluroinic acid, hydrated silica, hydroxypropyl chitosan, hydroxypropyl guar, karaya gum, kelp, locust bean gum, natto gum, potassium alginate, potassium carrageenan, propylene glycol alginate, sclerotium gum, sodium carboyxmethyl dextran, sodium carrageenan, tragacanth gum, xanthan gum, and mixtures thereof.

(v). Crosslinked Vinyl Ether/Maleic Anhydride Copolymers: Other additional thickening and gelling agents useful herein include crosslinked copolymers of alkyl vinyl ethers and maleic anhydride. In

these copolymers the vinyl ethers are represented by the formula R-O-CH==CH_2 wherein R is a C1-C6 alkyl group, preferably R is methyl. Preferred crosslinking agents are C4-C20 dienes, preferably C6 to C16 dienes, and most preferably C8 to C12 dienes. A particularly preferred copolymer is one formed from methyl vinyl ether and maleic anhydride wherein the copolymer has been crosslinked with decadiene, and wherein the polymer when diluted as a 0.5% aqueous solution at pH 7 at 25°C has a viscosity of 50,000-70,000 cps when measured using a Brookfield RTV viscometer, spindle #7 at 10 rpm. This copolymer has the CTFA designation PVM/MA decadiene crosspolymer and is commercially available as Stabileze™ 06 from International Specialty Products (Wayne NJ).

(vi). Crosslinked poly(N-vinylpyrrolidones): Crosslinked polyvinyl(N-pyrrolidones) additionally useful herein as thickening and gelling agents include those described in U.S. Patent No. 5,139,770, to Shih et al, issued August 18, 1992, and U.S. Patent No. 5,073,614, to Shih et al., issued December 17, 1991, both patents of which are incorporated by reference herein in their entirety. These gelling agents typically contain from about 0.25% to about 1% by weight of a crosslinking agent selected from the group consisting of divinyl ethers and diallyl ethers of terminal diols containing from about 2 to about 12 carbon atoms, divinyl ethers and diallyl ethers of polyethylene glycols containing from about 2 to about 600 units, dienes having from about 6 to about 20 carbon atoms, divinyl benzene, vinyl and allyl ethers of pentaerythritol, and the like. Typically, these gelling agents have a viscosity from about 25,000 cps to about 40,000 cps when measured as a 5% aqueous solution at 25°C using a Brookfield RVT viscometer with Spindle #6 at 10 rpm. Commercially available examples of these polymers include ACP-1120, ACP-1179, and ACP-1180, available from International Specialty Products (Wayne, NJ).

Thickening agents which are suitable for use herein also include those disclosed in U.S. Patent No., 4,387,107, to Klein et al., issued June 7, 1983 and "Encyclopedia of Polymer and Thickeners for Cosmetics," R.Y. Lochhead and W. R. Fron, eds., Cosmetics & Toiletries, vol. 108, pp. 95-135 (May 1993), which are all incorporated herein by reference in their entirety.

Preferred compositions of the present invention include a thickening agent selected from the group consisting of carboxylic acid polymers, acrylates/C_{10}-C_{30} alkyl acrylate crosspolymers, polyacrylamide polymers, and mixtures thereof. Generally, the thickening agent used to thicken the hydrophilic liquid carrier will preferably not be used in the acid form since acidic thickeners can interact with the charged reflective particulate material suspended or dispersed within the thickened hydrophilic phase. Alternatively, if the acid form of the thickening agents are used, the composition can be neutralized to a pH range described hereinafter before addition of the charged reflective particulate material. Generally, the pH of the thickened hydrophilic liquid carrier will range from about 4 to about 8.5, preferably from about 4.5 to about 8, more preferably from about 5 to 8, and most preferably from about 6 to 8.

III. OPTIONAL COMPOUNDS

The compositions herein may contain a wide variety of optional ingredients that perform one or more functions useful in products of this type. Such optional components may be found in either the

hydrophilic phase or the optional hydrophobic phase(s) or in one or more additional phases of the compositions herein. Nonexclusive examples of such materials are described in Harry's Cosmeticology, 7th Ed., Harry & Wilkinson (Hill Publishers, London 1982); in Pharmaceutical Dosage Forms- Disperse Systems; Lieberman, Rieger & Banker, Vols. 1 (1988) & 2 (1989); Marcel Decker, Inc.; in The Chemistry and Manufacture of Cosmetics, 2nd. Ed., deNavarre (Van Nostrand 1962-1965); and in The Handbook of Cosmetic Science and Technology, 1st Ed.. Knowlton & Pearce (Elsevier 1993). Such ingredients include, but are not limited to, transparent particulates; skin conditioning agents such as emollients, humectants, and moisturizers; skin cleansers; skin care actives such as vitamin B3 compounds, retinoids, anti-oxidants/radical scavengers, and organic hydroxy acids; structuring agents; and other actives including anti-inflammatory agents, sunscreens/sunblocks, chelators, desquamation agents/exfoliants, and skin lightening agents. Each of these functional optional ingredients is described in detail as follows:

1. Transparent Particles: A safe and effective amount of a transparent particle may be added to the compositions of the subject invention, preferably from about 0.1% to about 15%, more preferably from about 0.2% to about 5%, and most preferable from about 0.3% to about 2.5%. The transparent particles have a refractive index of less then about 2.0. These particles diffuse light instead of reflecting light. Nonlimiting examples include mica, silica, nylon, polyethylene, talc, styrene, polypropylene, ethylene/acrylic acid copolymer, sericite, aluminum oxide, silicone resin, barium sulfate, calcium carbonate, cellulose acetate, polymethyl methacrylate, and mixtures thereof. Nonlimiting examples of commercially available transparent particles include Kobo MSS-500 silica; Kobo EA-209 (ethylene/acrylic acid copolymer); and M-102-Mica available from U.S. Cosmetic Corp., located in Dayville, CT.

These transparent particles can also be treated with various treatments or made into a variety of composites to provide desired characteristics. A nonlimiting example of a commercially available composite transparent particle is Naturaleaf powder ® (composite of mica, barium sulfate, and TiO_2), available from EM Industries, located in Hawthorne, NY.

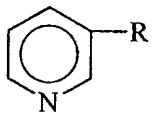
2. Skin Benefit Actives: In a preferred embodiment, the composition also includes one or more actives useful for chronically regulating skin condition. Such materials are those which manifest skin appearance benefits following chronic application of the composition containing such materials. Materials having this effect include, but are not limited to, Vitamin B_3 compounds, retinoids, anti-oxidants/radical scavengers, organic hydroxy acids and mixtures thereof.

Specific examples of skin benefit actives include the following.

(i) Vitamin B_3 Compounds: In a preferred embodiment, the compositions of the present invention comprise a safe and effective amount of a vitamin B_3 compound. The vitamin B_3 compound enhances the skin appearance benefits of the present invention, especially in regulating skin condition, including regulating signs of skin aging, more especially wrinkles, lines, and pores. The compositions of the present invention preferably comprise from about 0.01% to about 50%, more preferably from about

0.1% to about 10%, even more preferably from about 0.5% to about 10%, and still more preferably from about 1% to about 5%, most preferably from about 2% to about 5%, of the vitamin B_3 compound .

As used herein, "vitamin B_3 compound" means a compound having the formula:



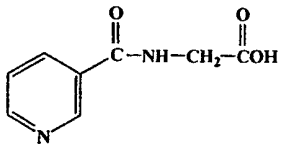
wherein R is - $CONH_2$ (i.e., niacinamide), - COOH (i.e., nicotinic acid) or - CH_2OH (i.e., nicotinyl alcohol); derivatives thereof; and salts of any of the foregoing.

Exemplary derivatives of the foregoing vitamin B_3 compounds include nicotinic acid esters, including non-vasodilating esters of nicotinic acid, nicotinyl amino acids, nicotinyl alcohol esters of carboxylic acids, nicotinic acid N-oxide and niacinamide N-oxide.

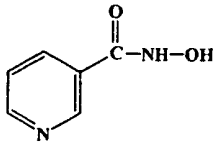
Suitable esters of nicotinic acid include nicotinic acid esters of C_1-C_{22}, preferably C_1-C_{16}, more preferably C_1-C_6 alcohols. The alcohols are suitably straight-chain or branched chain, cyclic or acyclic, saturated or unsaturated (including aromatic), and substituted or unsubstituted. The esters are preferably non-vasodilating. As used herein, "non-vasodilating" means that the ester does not commonly yield a visible flushing response after application to the skin in the subject compositions (the majority of the general population would not experience a visible flushing response, although such compounds may cause vasodilation not visible to the naked eye, i.e., the ester is non-rubifacient). Non-vasodilating esters of nicotinic acid include tocopherol nicotinate and inositol hexanicotinate; tocopherol nicotinate is preferred.

Other derivatives of the vitamin B_3 compound are derivatives of niacinamide resulting from substitution of one or more of the amide group hydrogens. Nonlimiting examples of derivatives of niacinamide useful herein include nicotinyl amino acids, derived, for example, from the reaction of an activated nicotinic acid compound (e.g., nicotinic acid azide or nicotinyl chloride) with an amino acid, and nicotinyl alcohol esters of organic carboxylic acids (e.g., C1 - C18). Specific examples of such derivatives include nicotinuric acid ($C_8H_8N_2O_3$) and nicotinyl hydroxamic acid ($C_6H_6N_2O_2$), which have the following chemical structures:

nicotinuric acid:



nicotinyl hydroxamic acid:



Exemplary nicotinyl alcohol esters include nicotinyl alcohol esters of the carboxylic acids salicylic acid, acetic acid, glycolic acid, palmitic acid and the like. Other non-limiting examples of vitamin B_3 compounds useful herein are 2-chloronicotinamide, 6-aminonicotinamide, 6-methylnicotinamide, n-methyl-nicotinamide, n,n-diethylnicotinamide, n-(hydroxymethyl)-nicotinamide, quinolinic acid imide, nicotinanilide, n-benzylnicotinamide, n-ethylnicotinamide, nifenazone, nicotinaldehyde, isonicotinic acid, methyl isonicotinic acid, thionicotinamide, nialamide, 1-(3-pyridylmethyl) urea, 2-mercaptonicotinic acid, nicomol, and niaprazine.

Examples of the above vitamin B_3 compounds are well known in the art and are commercially available from a number of sources, e.g., the Sigma Chemical Company (St. Louis, MO); ICN Biomedicals, Inc. (Irvin, CA) and Aldrich Chemical Company (Milwaukee, WI).

One or more vitamin B_3 compounds may be used herein. Preferred vitamin B_3 compounds are niacinamide and tocopherol nicotinate. Niacinamide is more preferred.

When used, salts, derivatives, and salt derivatives of niacinamide are preferably those having substantially the same efficacy as niacinamide in the methods of regulating skin condition described herein.

Salts of the vitamin B_3 compound are also useful herein. Nonlimiting examples of salts of the vitamin B_3 compound useful herein include organic or inorganic salts, such as inorganic salts with anionic inorganic species (e.g., chloride, bromide, iodide, carbonate, preferably chloride), and organic carboxylic acid salts (including mono-, di- and tri- C1 - C18 carboxylic acid salts, e.g., acetate, salicylate, glycolate, lactate, malate, citrate, preferably monocarboxylic acid salts such as acetate). These and other salts of the vitamin B_3 compound can be readily prepared by the skilled artisan, for example, as described by W. Wenner, "The Reaction of L-Ascorbic and D-Iosascorbic Acid with Nicotinic Acid and Its Amide", J. Organic Chemistry, Vol. 14, 22-26 (1949), which is incorporated herein by reference. Wenner describes the synthesis of the ascorbic acid salt of niacinamide.

In a preferred embodiment, the ring nitrogen of the vitamin B_3 compound is substantially chemically free (e.g., unbound and/or unhindered), or after delivery to the skin becomes substantially chemically free ("chemically free" is hereinafter alternatively referred to as "uncomplexed"). More preferably, the vitamin B_3 compound is essentially uncomplexed. Therefore, if the composition contains the vitamin B_3 compound in a salt or otherwise complexed form, such complex is preferably substantially reversible, more preferably essentially reversible, upon delivery of the composition to the skin. For example, such complex should be substantially reversible at a pH of from about 5.0 to about 6.0. Such reversibility can be readily determined by one having ordinary skill in the art.

More preferably the vitamin B_3 compound is substantially uncomplexed in the composition prior to delivery to the skin. Exemplary approaches to minimizing or preventing the formation of undesirable complexes include omission of materials which form substantially irreversible or other complexes with the vitamin B_3 compound, pH adjustment, ionic strength adjustment, the use of surfactants, and formulating

wherein the vitamin B_3 compound and materials which complex therewith are in different phases. Such approaches are well within the level of ordinary skill in the art.

Thus, in a preferred embodiment, the vitamin B_3 compound contains a limited amount of the salt form and is more preferably substantially free of salts of a vitamin B_3 compound. Preferably the vitamin B_3 compound contains less than about 50% of such salt, and is more preferably essentially free of the salt form. The vitamin B_3 compound in the compositions hereof having a pH of from about 4 to about 7 typically contain less than about 50% of the salt form.

The vitamin B_3 compound may be included as the substantially pure material, or as an extract obtained by suitable physical and/or chemical isolation from natural (e.g., plant) sources. The vitamin B_3 compound is preferably substantially pure, more preferably essentially pure.

(ii) Retinoids: In a preferred embodiment, the compositions of the present invention contain a retinoid. The retinoid enhances the skin appearance benefits of the present invention, especially in regulating skin condition, including regulating signs of skin aging, more especially wrinkles, lines, and pores.

As used herein, "retinoid" includes all natural and/or synthetic analogs of Vitamin A or retinol-like compounds which possess the biological activity of Vitamin A in the skin as well as the geometric isomers and stereoisomers of these compounds. The retinoid is preferably retinol, retinol esters (e.g., C_2 - C_{22} alkyl esters of retinol, including retinyl palmitate, retinyl acetate, retinyl propionate), retinal, and/or retinoic acid (including all-trans retinoic acid and/or 13-cis-retinoic acid), more preferably retinoids other than retinoic acid. These compounds are well known in the art and are commercially available from a number of sources, e.g., Sigma Chemical Company (St. Louis, MO), and Boerhinger Mannheim (Indianapolis, IN). Other retinoids which are useful herein are described in U.S. Patent Nos. 4,677,120, issued Jun. 30, 1987 to Parish et al.; 4,885,311, issued Dec. 5, 1989 to Parish et al.; 5,049,584, issued Sep. 17, 1991 to Purcell et al.; 5,124,356, issued Jun. 23, 1992 to Purcell et al.; and Reissue 34,075, issued Sep. 22, 1992 to Purcell et al.. Other suitable retinoids are tocopheryl-retinoate [tocopherol ester of retinoic acid (trans- or cis-), adapalene {6-[3-(1-adamantyl)-4-methoxyphenyl]-2-naphthoic acid}, and tazarotene (ethyl 6-[2-(4,4-dimethylthiochroman-6-yl)-ethynyl]nicotinate). One or more retinoids may be used herein. Preferred retinoids are retinol, retinyl palmitate, retinyl acetate, retinyl proprionate, retinal and combinations thereof. More preferred are retinol and retinyl palmitate.

The retinoid may be included as the substantially pure material, or as an extract obtained by suitable physical and/or chemical isolation from natural (e.g., plant) sources. The retinoid is preferably substantially pure, more preferably essentially pure.

The compositions of this invention may contain a safe and effective amount of the retinoid, such that the resultant composition is safe and effective for regulating skin condition, preferably for regulating visible and/or tactile discontinuities in skin, more preferably for regulating signs of skin aging, even more preferably for regulating visible and/or tactile discontinuities in skin texture associated with skin aging.

The compositions preferably contain from or about 0.005% to or about 2%, more preferably 0.01% to or about 2%, retinoid. Retinol is most preferably used in an amount of from or about 0.01% to or about 0.15%; retinol esters are most preferably used in an amount of from or about 0.01% to or about 2% (e.g., about 1%); retinoic acids are most preferably used in an amount of from or about 0.01% to or about 0.25%; tocopheryl-retinoate, adapalene, and tazarotene are most preferably used in an amount of from or about 0.01% to or about 2%.

In a preferred embodiment, the composition contains both a retinoid and a Vitamin B_3 compound. The retinoid is preferably used in the above amounts, and the vitamin B_3 compound is preferably used in an amount of from or about 0.1% to or about 10%, more preferably from or about 2% to or about 5%.

(iii) Anti-Oxidants/Radical Scavengers: Preferred compositions of the subject invention include an anti-oxidant/radical scavenger. The anti-oxidant/radical scavenger is especially useful for providing protection against UV radiation which can cause increased scaling or texture changes in the stratum corneum and against other environmental agents which can cause skin damage.

A safe and effective amount of an anti-oxidant/radical scavenger may be added to the compositions of the subject invention, preferably from about 0.1% to about 10%, more preferably from about 1% to about 5%, of the composition.

Anti-oxidants/radical scavengers such as ascorbic acid (vitamin C) and its salts, ascorbyl esters of fatty acids, ascorbic acid derivatives (e.g., magnesium ascorbyl phosphate), tocopherol (vitamin E), tocopherol sorbate, tocopherol acetate, other esters of tocopherol, butylated hydroxy benzoic acids and their salts, 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (commercially available under the tradename Trolox^R), gallic acid and its alkyl esters, especially propyl gallate, uric acid and its salts and alkyl esters, sorbic acid and its salts, amines (e.g., N,N-diethylhydroxylamine, amino-guanidine), sulfhydryl compounds (e.g., glutathione), dihydroxy fumaric acid and its salts, lycine pidolate, arginine pilolate, nordihydroguaiaretic acid, bioflavonoids, lysine, methionine, proline, superoxide dismutase, silymarin, tea extracts, grape skin/seed extracts, melanin, and rosemary extracts may be used. Preferred anti-oxidants/radical scavengers are selected from tocopherol sorbate and other esters of tocopherol, more preferably tocopherol sorbate. For example, the use of tocopherol sorbate in topical compositions and applicable to the present invention is described in U.S. Patent No. 4,847,071, issued on July 11, 1989 to Donald L. Bissett, Rodney D. Bush and Ranjit Chatterjee, incorporated herein by reference.

(iv) Organic Hydroxy Acids: Compositions of the present invention may comprise an organic hydroxy acid. Suitable hydroxy acids include C_1 - C_{18} hydroxy acids, preferably C_8 or below. The hydroxy acids can be substituted or unsubstituted, straight chain, branched chain or cyclic (preferably straight chain), and saturated or unsaturated (mono- or poly- unsaturated) (preferably saturated). Non-limiting examples of suitable hydroxy acids include salicylic acid, glycolic acid, lactic acid, 5 octanoyl salicylic acid, hydroxyoctanoic acid, hydroxycaprylic acid, and lanolin fatty acids. Preferred

concentrations of the organic hydroxy acid range from about 0.1% to about 10%, more preferably from about 0.2% to about 5%, also preferably from about 0.5% to about 2%. Salicylic acid is preferred. The organic hydroxy acids enhance the skin appearance benefits of the present invention. For example, the organic hydroxy acids tend to improve the texture of the skin.

3. Water Soluble Skin Conditioning Compounds: Preferred compositions of the invention can also comprise one or more water soluble skin conditioning compounds. Water soluble skin conditioning compounds are useful for lubricating the skin, increasing the smoothness and suppleness of the skin, preventing or relieving dryness of the skin, hydrating the skin, and/or protecting the skin. Water soluble skin conditioning compounds enhance the dry skin appearance improvements of the present invention, including but not limited to essentially immediate visual improvements in skin appearance. The water soluble skin conditioning compounds are preferably selected from the group consisting of humectants, moisturizers and mixtures thereof. The water soluble skin conditioning compounds are preferably present at a level of at least about 0.1%, more preferably from about 1% to about 99.99%, even more preferably from about 1% to about 50%, still more preferably from about 2% to about 30% and most preferably from about 5% to about 25% (e.g., about 5% to about 15%).

Nonlimiting examples of water soluble conditioning compounds include those selected from the group consisting of polyhydric alcohols, polypropylene glycols, dipropylene glycol, polyethylene glycols, ureas, pyrolidone carboxylic acids, ethoxylated and/or propoxylated C3-C6 diols and triols, alpha-hydroxy C2-C6 carboxylic acids, ethoxylated and/or propoxylated sugars, sugars having up to about 12 carbons atoms, sugar alcohols having up to about 12 carbon atoms, and mixtures thereof. Specific examples of useful water soluble conditioning agents include materials such as urea; guanidine; glycolic acid and glycolate salts (e.g. ammonium and quaternary alkyl ammonium); lactic acid and lactate salts (e.g. ammonium and quaternary alkyl ammonium); sucrose, fructose, glucose, eruthrose, erythritol, sorbitol, hydroxypropyl sorbitol, mannitol, glycerol, hexane triol, propylene glycol, butylene glycol, hexylene glycol, threitol, pentaerythritol, xylitol, glucitol, and the like; polyethylene glycols such as PEG-2, PEG-3, PEG-30, PEG-50, polypropylene glycols such as PPG-9, PPG-12, PPG-15, PPG-17, PPG-20, PPG-26, PPG-30, PPG-34; alkoxylated glucose; hyaluronic acid; and mixtures thereof. Also useful are materials such as aloe vera in any of its variety of forms (e.g., aloe vera gel); lactamide monoethanolamine; acetamide monoethanolamine; panthenol; and mixtures thereof. Also useful are ethoxylated glycerols and propoxylated glycerols as described in U.S. Patent No. 4,976,953, to Orr et al., issued December 11, 1990, which is incorporated by reference herein in its entirety.

4. Structuring Agents: The compositions hereof, and especially the emulsions hereof, may contain a structuring agent. Structuring agents are particularly preferred in the oil-in-water emulsions of the present invention. Without being limited by theory, it is believed that the structuring agent assists in providing rheological characteristics to the composition which contribute to the stability of the composition. For example, the structuring agent tends to assist in the formation of the liquid crystalline

gel network structures. The structuring agent may also function as an emulsifier or surfactant. Preferred compositions of this invention comprise from about 1% to about 20%, more preferably from about 1% to about 10%, most preferably from about 2% to about 9%, of one or more structuring agents.

Preferred structuring agents are those having an HLB of from about 1 to about 8 and having a melting point of at least about 45°C. Suitable structuring agents are those selected from the group consisting of saturated C_{14} to C_{30} fatty alcohols, saturated C_{16} to C_{30} fatty alcohols containing from about 1 to about 5 moles of ethylene oxide, saturated C_{16} to C_{30} diols, saturated C_{16} to C_{30} monoglycerol ethers, saturated C_{16} to C_{30} hydroxy fatty acids, C_{14} to C_{30} hydroxylated and nonhydroxylated saturated fatty acids, C_{14} to C_{30} saturated ethoxylated fatty acids, amines and alcohols containing from about 1 to about 5 moles of ethylene oxide diols, C_{14} to C_{30} saturated glyceryl mono esters with a monoglyceride content of at least 40%, C_{14} to C_{30} saturated polyglycerol esters having from about 1 to about 3 alkyl group and from about 2 to about 3 saturated glycerol units, C_{14} to C_{30} glyceryl mono ethers, C_{14} to C_{30} sorbitan mono/diesters, C_{14} to C_{30} saturated ethoxylated sorbitan mono/diesters with about 1 to about 5 moles of ethylene oxide, C_{14} to C_{30} saturated methyl glucoside esters, C_{14} to C_{30} saturated sucrose mono/diesters, C_{14} to C_{30} saturated ethoxylated methyl glucoside esters with about 1 to about 5 moles of ethylene oxide, C_{14} to C_{30} saturated polyglucosides having an average of between 1 to 2 glucose units and mixtures thereof, having a melting point of at least about 45°C.

The preferred structuring agents of the present invention are selected from the group consisting of stearic acid, palmitic acid, stearyl alcohol, cetyl alcohol, behenyl alcohol, stearic acid, palmitic acid, the polyethylene glycol ether of stearyl alcohol having an average of about 1 to about 5 ethylene oxide units, the polyethylene glycol ether of cetyl alcohol having an average of about 1 to about 5 ethylene oxide units, and mixtures thereof. More preferred structuring agents of the present invention are selected from the group consisting of stearyl alcohol, cetyl alcohol, behenyl alcohol, the polyethylene glycol ether of stearyl alcohol having an average of about 2 ethylene oxide units (steareth-2), the polyethylene glycol ether of cetyl alcohol having an average of about 2 ethylene oxide units, and mixtures thereof. Even more preferred structuring agents are selected from the group consisting of stearic acid, palmitic acid, stearyl alcohol, cetyl alcohol, behenyl alcohol, steareth-2, and mixtures thereof.

5. Anti-Inflammatory Agents: A safe and effective amount of an anti-inflammatory agent may be added to the compositions of the subject invention, preferably from about 0.1% to about 10%, more preferably from about 0.5% to about 5%, of the composition. The anti-inflammatory agent enhances the skin appearance benefits of the present invention, e.g., such agents contribute to a more uniform and acceptable skin tone or color. The exact amount of anti-inflammatory agent to be used in the compositions will depend on the particular anti-inflammatory agent utilized since such agents vary widely in potency.

Steroidal anti-inflammatory agents, including but not limited to, corticosteroids such as hydrocortisone, hydroxyltriamcinolone, alpha-methyl dexamethasone, dexamethasone-phosphate, beclomethasone dipropionates, clobetasol valerate, desonide, desoxymethasone, desoxycorticosterone

acetate, dexamethasone, dichlorisone, diflorasone diacetate, diflucortolone valerate, fluadrenolone, fluclorolone acetonide, fludrocortisone, flumethasone pivalate, fluosinolone acetonide, fluocinonide, flucortine butylesters, fluocortolone, fluprednidene (fluprednylidene) acetate, flurandrenolone, halcinonide, hydrocortisone acetate, hydrocortisone butyrate, methylprednisolone, triamcinolone acetonide, cortisone, cortodoxone, flucetonide, fludrocortisone, difluorosone diacetate, fluradrenolone, fludrocortisone, diflurosone diacetate, fluradrenolone acetonide, medrysone, amcinafel, amcinafide, betamethasone and the balance of its esters, chloroprednisone, chlorprednisone acetate, clocortelone, clescinolone, dichlorisone, diflurprednate, flucloronide, flunisolide, fluoromethalone, fluperolone, fluprednisolone, hydrocortisone valerate, hydrocortisone cyclopentylpropionate, hydrocortamate, meprednisone, paramethasone, prednisolone, prednisone, beclomethasone dipropionate, triamcinolone, and mixtures thereof may be used. The preferred steroidal anti-inflammatory for use is hydrocortisone.

A second class of anti-inflammatory agents which is useful in the compositions includes the nonsteroidal anti-inflammatory agents. The variety of compounds encompassed by this group are well-known to those skilled in the art. For detailed disclosure of the chemical structure, synthesis, side effects, etc. of non-steroidal anti-inflammatory agents, reference may be had to standard texts, including Anti-inflammatory and Anti-Rheumatic Drugs, K. D. Rainsford, Vol. I-III, CRC Press, Boca Raton, (1985), and Anti-inflammatory Agents, Chemistry and Pharmacology, 1, R. A. Scherrer, et al., Academic Press, New York (1974), each incorporated herein by reference.

Specific non-steroidal anti-inflammatory agents useful in the composition invention include, but are not limited to:

1) the oxicams, such as piroxicam, isoxicam, tenoxicam, sudoxicam, and CP-14,304;
2) the salicylates, such as aspirin, disalcid, benorylate, trilisate, safapryn, solprin, diflunisal, and fendosal;
3) the acetic acid derivatives, such as diclofenac, fenclofenac, indomethacin, sulindac, tolmetin, isoxepac, furofenac, tiopinac, zidometacin, acematacin, fentiazac, zomepirac, clindanac, oxepinac, felbinac, and ketorolac;
4) the fenamates, such as mefenamic, meclofenamic, flufenamic, niflumic, and tolfenamic acids;
5) the propionic acid derivatives, such as ibuprofen, naproxen, benoxaprofen, flurbiprofen, ketoprofen, fenoprofen, fenbufen, indopropfen, pirprofen, carprofen, oxaprozin, pranoprofen, miroprofen, tioxaprofen, suprofen, alminoprofen, and tiaprofenic; and
6) the pyrazoles, such as phenylbutazone, oxyphenbutazone, feprazone, azapropazone, and trimethazone.

Mixtures of these non-steroidal anti-inflammatory agents may also be employed, as well as the dermatologically acceptable salts and esters of these agents. For example, etofenamate, a flufenamic acid derivative, is particularly useful for topical application. Of the nonsteroidal anti-inflammatory agents,

ibuprofen, naproxen, flufenamic acid, etofenamate, aspirin, mefenamic acid, meclofenamic acid, piroxicam and felbinac are preferred; ibuprofen, naproxen, etofenamate, aspirin and flufenamic acid are most preferred.

Finally, so-called "natural" anti-inflammatory agents are useful in methods of the subject invention. Such agents may suitably be obtained as an extract by suitable physical and/or chemical isolation from natural sources (e.g., plants, fungi, by-products of microorganisms). For example, candelilla wax, alpha bisabolol, aloe vera, Manjistha (extracted from plants in the genus Rubia, particularly Rubia Cordifolia), and Guggal (extracted from plants in the genus Commiphora, particularly Commiphora Mukul), kola extract, chamomile, and sea whip extract, may be used.

Additional anti-inflammatory agents useful herein include compounds of the Licorice (the plant genus/species Glycyrrhiza glabra) family, including glycyrrhetic acid, glycyrrhizic acid, and derivatives thereof (e.g., salts and esters). Suitable salts of the foregoing compounds include metal and ammonium salts. Suitable esters include C_2 - C_{24} saturated or unsaturated esters of the acids, preferably C_{10} - C_{24}, more preferably C_{16} - C_{24}. Specific examples of the foregoing include oil soluble licorice extract, the glycyrrhizic and glycyrrhetic acids themselves, monoammonium glycyrrhizinate, monopotassium glycyrrhizinate, dipotassium glycyrrhizinate, 1-beta-glycyrrhetic acid, stearyl glycyrrhetinate, and 3-stearyloxy-glycyrrhetinic acid, and disodium 3-succinyloxy-beta-glycyrrhetinate. Stearyl glycyrrhetinate is preferred.

6. Sunscreens and Sunblocks: Exposure to ultraviolet light can result in excessive scaling and texture changes of the stratum corneum. Therefore, the compositions of the subject invention preferably contain a sunscreen or sunblock. Suitable sunscreens or sunblocks may be organic or inorganic.

A wide variety of conventional sunscreening agents are suitable for use herein. Sagarin, et al., at Chapter VIII, pages 189 et seq., of Cosmetics Science and Technology (1972), discloses numerous suitable agents, and is incorporated herein by reference. Specific suitable sunscreening agents include, for example: p-aminobenzoic acid, its salts and its derivatives (ethyl, isobutyl, glyceryl esters; p-dimethylaminobenzoic acid); anthranilates (i.e., o-amino-benzoates; methyl, menthyl, phenyl, benzyl, phenylethyl, linalyl, terpinyl, and cyclohexenyl esters); salicylates (amyl, phenyl, octyl, benzyl, menthyl, glyceryl, and di-pro-pyleneglycol esters); cinnamic acid derivatives (menthyl and benzyl esters, a-phenyl cinnamonitrile; butyl cinnamoyl pyruvate); dihydroxycinnamic acid derivatives (umbelliferone, methylumbelliferone, methylaceto-umbelliferone); trihydroxy-cinnamic acid derivatives (esculetin, methylesculetin, daphnetin, and the glucosides, esculin and daphnin); hydrocarbons (diphenylbutadiene, stilbene); dibenzalacetone and benzalacetophenone; naphtholsulfonates (sodium salts of 2-naphthol-3,6-disulfonic and of 2-naphthol-6,8-disulfonic acids); di-hydroxynaphthoic acid and its salts; o- and p-hydroxybiphenyldisulfonates; coumarin derivatives (7-hydroxy, 7-methyl, 3-phenyl); diazoles (2-acetyl-3-bromoindazole, phenyl benzoxazole, methyl naphthoxazole, various aryl benzothiazoles); quinine salts (bisulfate, sulfate, chloride, oleate, and tannate); quinoline derivatives (8-hydroxyquinoline salts, 2-

phenylquinoline); hydroxy- or methoxy-substituted benzophenones; uric and violuric acids; tannic acid and its derivatives (e.g., hexaethylether); (butyl carbotol) (6-propyl piperonyl) ether; hydroquinone; benzophenones (oxybenzene, sulisobenzone, dioxybenzone, benzoresorcinol, 2,2',4,4'-tetrahydroxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone, octabenzone; 4-isopropyldibenzoylmethane; butylmethoxydibenzoylmethane; etocrylene; octocrylene; [3-(4'-methylbenzylidene bornan-2-one) and 4-isopropyl-di-benzoylmethane.

Of these, 2-ethylhexyl-p-methoxycinnamate (commercially available as PARSOL MCX), 4,4'-t-butyl methoxydibenzoyl-methane (commercially available as PARSOL 1789), 2-hydroxy-4-methoxybenzophenone, octyldimethyl-p-aminobenzoic acid, digalloyltrioleate, 2,2-dihydroxy-4-methoxybenzophenone, ethyl-4-(bis(hydroxy-propyl))aminobenzoate, 2-ethylhexyl-2-cyano-3,3-diphenylacrylate, 2-ethylhexyl-salicylate, glyceryl-p-aminobenzoate, 3,3,5-tri-methylcyclohexylsalicylate, methylanthranilate, p-dimethyl-aminobenzoic acid or aminobenzoate, 2-ethylhexyl-p-dimethyl-amino-benzoate, 2-phenylbenzimidazole-5-sulfonic acid, 2-(p-dimethylaminophenyl)-5-sulfonicbenzoxazoic acid, octocrylene and mixtures of these compounds, are preferred.

More preferred organic sunscreens useful in the compositions useful in the subject invention are 2-ethylhexyl-p-methoxycinnamate, butylmethoxydibenzoyl-methane, 2-hydroxy-4-methoxybenzo-phenone, 2-phenylbenzimidazole-5-sulfonic acid, octyldimethyl-p-aminobenzoic acid, octocrylene and mixtures thereof.

Also particularly useful in the compositions are sunscreens such as those disclosed in U.S. Patent No. 4,937,370 issued to Sabatelli on June 26, 1990, and U.S. Patent No. 4,999,186 issued to Sabatelli & Spirnak on March 12, 1991, both of which are incorporated herein by reference. The sunscreening agents disclosed therein have, in a single molecule, two distinct chromophore moieties which exhibit different ultra-violet radiation absorption spectra. One of the chromophore moieties absorbs predominantly in the UVB radiation range and the other absorbs strongly in the UVA radiation range.

Preferred members of this class of sunscreening agents are 4-N,N-(2-ethylhexyl)methyl-aminobenzoic acid ester of 2,4-dihydroxybenzophenone; N,N-di-(2-ethylhexyl)-4-aminobenzoic acid ester with 4-hydroxydibenzoylmethane; 4-N,N-(2-ethylhexyl)methyl-aminobenzoic acid ester with 4-hydroxydibenzoylmethane; 4-N,N-(2-ethylhexyl)methyl-aminobenzoic acid ester of 2-hydroxy-4-(2-hydroxyethoxy)benzophenone; 4-N,N-(2-ethylhexyl)-methylaminobenzoic acid ester of 4-(2-hydroxyethoxy)dibenzoylmethane; N,N-di-(2-ethylhexyl)-4-aminobenzoic acid ester of 2-hydroxy-4-(2-hydroxyethoxy)benzophenone; and N,N-di-(2-ethylhexyl)-4-aminobenzoic acid ester of 4-(2-hydroxyethoxy)dibenzoylmethane and mixtures thereof.

Especially preferred sunscreens or sunblocks include butylmethoxydibenzoylmethane, 2-ethylhexyl-p-methoxycinnamate, phenyl benzimidazole sulfonic acid, and octocrylene.

A safe and effective amount of the sunscreen or sunblock is used, typically from about 1% to about 20%, more typically from about 2% to about 10%. Exact amounts will vary depending upon the sunscreen chosen and the desired Sun Protection Factor (SPF).

An agent may also be added to any of the compositions useful in the subject invention to improve the skin substantivity of those compositions, particularly to enhance their resistance to being washed off by water, or rubbed off. A preferred agent which will provide this benefit is a copolymer of ethylene and acrylic acid. Compositions comprising this copolymer are disclosed in U.S. Patent 4,663,157, Brock, issued May 5, 1987, which is incorporated herein by reference.

7. Chelators: As used herein, "chelating agent" means an active agent capable of removing a metal ion from a system by forming a complex so that the metal ion cannot readily participate in or catalyze chemical reactions. The inclusion of a chelating agent is especially useful for providing protection against UV radiation which can contribute to excessive scaling or skin texture changes and against other environmental agents which can cause skin damage.

A safe and effective amount of a chelating agent may be added to the compositions of the subject invention, preferably from about 0.1% to about 10%, more preferably from about 1% to about 5%, of the composition. Exemplary chelators that are useful herein are disclosed in U.S. Patent No. 5,487,884, issued 1/30/96 to Bissett et al.; International Publication No. 91/16035, Bush et al., published 10/31/95; and International Publication No. 91/16034, Bush et al., published 10/31/95; all incorporated herein by reference. Preferred chelators useful in compositions of the subject invention are furildioxime and derivatives thereof.

8. Desquamation Agents/Exfoliants: A safe and effective amount of a desquamation agent may be added to the compositions of the subject invention, more preferably from about 0.1% to about 10%, even more preferably from about 0.2% to about 5%, also preferably from about 0.5% to about 4% of the composition. Desquamation agents enhance the skin appearance benefits of the present invention. For example, the desquamation agents tend to improve the texture of the skin (e.g., smoothness). A variety of desquamation agents are known in the art and are suitable for use herein, including but not limited to the organic hydroxy agents described above. One desquamation system that is suitable for use herein comprises sulfhydryl compounds and zwitterionic surfactants and is described in copending application Serial No. 08/480,632, filed on June 7, 1995 in the name of Donald L. Bissett, corresponding to PCT Application No. U.S. 95/08136, filed 6/29/95, each incorporated herein by reference. Another desquamation system that is suitable for use herein comprises salicylic acid and zwitterionic surfactants and is described in copending patent application Serial No. 08/554,944, filed on November 13, 1995 as a continuation of Serial No. 08/209,401, filed on March 9, 1994 in the name of Bissett, corresponding to PCT Application No. 94/12745, filed 11/4/94, published 5/18/95, each incorporated herein by reference. Zwitterionic surfactants such as described in these applications are also useful as desquamatory agents herein, with cetyl betaine being particularly preferred.

9. Skin Lightening Agents: The compositions of the present invention may comprise a skin lightening agent. When used, the compositions preferably comprise from about 0.1% to about 10%, more preferably from about 0.2% to about 5%, also preferably from about 0.5% to about 2%, of a skin lightening agent. Suitable skin lightening agents include those known in the art, including kojic acid, arbutin, ascorbic acid and derivatives thereof, e.g., magnesium ascorbyl phosphate. Skin lightening agents suitable for use herein also include those described in copending patent application Serial No. 08/479,935, filed on June 7, 1995 in the name of Hillebrand, corresponding to PCT Application No. U.S. 95/07432, filed 6/12/95; and copending patent application Serial No. 08/390,152, filed on February 24, 1995 in the names of Kalla L. Kvalnes, Mitchell A. DeLong, Barton J. Bradbury, Curtis B. Motley, and John D. Carter, corresponding to PCT Application No. U.S. 95/02809, filed 3/1/95, published 9/8/95; all incorporated herein by reference.

IV. INTRINSIC CHRONIC EFFICACY

The hydrophobic, metal ion chelators used in the present invention preferably exhibit an Intrinsic Chronic Efficacy of greater than about 33%, preferably 35%, more preferably 40%, and most preferably 45%. The Intrinsic Chronic Efficacy is a normalized measurement of the improvement of the appearance of dry skin on female legs (the region located away from the midline of the body and between the knee and the ankles) upon four successive treatments over a five day period. A description of the testing methodology to obtain Intrinsic Chronic Efficacy data follows:

Female panelists (18-55 years of age) were screened to identify individuals having dry skin on their legs (either naturally occurring or induced by washing with Lux bar soap). Assessment of the degree of skin dryness was accomplished by expert examiners (dermatology clinicians who run dermatology test clinics) using a 0-6 point scale. The clinical skin grading methodology and techniques published in Lukacovic et al, "Forearm Wash Test to Evaluate the Clinical Mildness of Cleansing Products," *J. Soc. Cosmet. Chem.*, Vol. 38, Pages 355-366(1988), which reference is incorporated herein in its entirety, was adapted to clinically grade the dry skin located on the outer regions (away from the midline of the body) of the lower extremeties of females (e.g., the outside area of skin between the knee and the ankles of the leg). The clinical grading scale is described below in Table I.

Table I. Leg Grading Scale

Grade	Skin dryness
0	No signs of dryness are present.
1.0	Patches of slight powderiness and occasional patches of small scales may be seen. Distribution is generalized.
2.0	Generalized slight powderiness are visible. Early cracking or occasional small lifting scales may be present
3.0	Generalized moderate powderiness and/or heavy cracking and lifting scales are present.
4.0	Generalized heavy powderiness and/or heavy cracking and lifting of scales are present.
5.0	Generalized high cracking and lifting scales are visible. Eczematous change may be present. Powderiness may be present but not prominent. May see bleeding

	cracks.
6.0	Generalized severe cracking are visible. Eczematous change may by present. Bleeding cracks may be present. Large scales may be beginning to disappear.

- Non-generalized: No more than 50% of the surface area of the leg exhibits attribute.
- Generalized: More than 50% of the surface area of the leg exhibits attribute.
- Whole units reflect generalized condition. Half units may be used in grade assessments to reflect non-generalized condition.

The test is conducted for five days, typically beginning on Monday and ending on Friday. The dry skin appearance of the panelists is assessed on the first day before the first treatment. This initial assessment is designated the Initial Grade. Each successive dry skin appearance grade is then assessed 24 hours after the last treatment and prior to each successive treatment (e.g., $Grade_{Day2}$, $Grade_{Day3}$, $Grade_{Day4}$, $Grade_{Day5}$). In addition to the dry skin appearance grades for the treated sites on the leg, dry skin appearance grades are also assessed for a predetermined untreated site on the leg at the same time as the assessments on the treated sites so that the results may be normalized. Dry skin appearance grades are assessed by the same trained examiner with the aid of a Luxo Illuminated Magnifying Lamp (Model KFM-1A) which provided 2.75X magnification and which had a shadow-free circular fluorescent light source (General Electric Cool White, 22 watt 8" Circline).

The treatment solution, which contains the skin active component, is applied once per day during the treatment period (e.g., Day 1 - Day 4) at the rate of 30 μL per 12.5 cm^2. Treatment solutions contain five weight percent of the skin active component in a volatile alcoholic vehicle comprising 50% ethanol, 25% propylene gycol, and 25% water. The treatment solution is spread over the treatment site with a gloved finger until the solution is absorbed into the skin.

Each grade is then converted into a Percent Improvement (PI) over the Initial Grade in the following manner: $PI_{Day\#} = ((\text{Initial Grade} - Grade_{Day\#})/\text{Initial Grade}) \times 100$

The Average Percent Improvement (API) is then calculated in the following manner:

$$API = (PI_{Day\,2} + PI_{Day\,3} + PI_{Day\,4} + PI_{Day\,5})/4$$

This API is then normalized by taking away any influences from the environment (e.g., warmer weather or higher humidity) by subtracting the API for a site on the leg which had not been treated. This normalization allows comparison of data between tests conducted at different times of the year. The calculation for the Intrinsic Chronic Efficacy is then determined in the following manner:

$$\text{Intrisic Chronic Efficacy} = API_{treatment} - API_{no\ treament}$$

VII METHODS FOR IMPROVING THE APPEARANCE OF DRY SKIN; FOR DESQUAMATING THE SKIN; AND FOR REGULATING THE VISIBLE AND TACTILE DISCONTINUITIES OF THE SKIN

The compounds of the present invention and compositions containing such compounds are useful for (i) improving the appearance of dry mammalian skin, (ii) desquamating mammalian skin, and (iii) regulating visible and/or tactile discontinuities in skin, e.g., visible and/or tactile discontinuities in skin texture, more especially discontinuities associated with skin aging. As described hereinbefore and without

being limited by theory, it is believed that these hydrophobic, metal ion chelators effectively penetrate into the superficial layers of the skin and enhance or maintain the normal process of desquamation in mammalian skin. Chronic use of the compositions of the present invention, therefore, naturally repairs the integrity of the natural moisture barrier function of the epidermal layer. In addition, by enhancing the natural process of desquamation, the compositions of the present invention are also useful for regulating the visible and/or tactile discontinuities in skin. The compounds herein described and compositions containing these compounds provide a visible improvement in the appearance of dry skin essentially after about one day following application of the composition to the skin.

A wide range of quantities of the compositions of the present invention can be employed to provide a skin appearance and/or feel benefit. Quantities of the present compositions which are typically applied per application are, in mg composition/cm^2 skin, from about 0.1 mg/cm^2 to about 10 mg/cm^2. A particularly useful application amount is about 2 mg/cm^2. Typically applications would be on the order of about once per day. However application rates can vary from about once per week up to about three times per day or more.

"Chronic topical application" and involves continued topical application of the composition over an extended period during the subject's lifetime, preferably for a period of at least about one week, more preferably for a period of at least about one month, even more preferably for at least about three months, even more preferably still for at least about six months, and most preferably for at least about one year. Chronic improvement of the appearance of dry skin results from following multiple topical applications of the composition to the skin. While benefits are obtainable after various maximum periods of use (e.g., five, ten or twenty years), it is preferred that chronic application continue throughout the subject's lifetime. Typically applications would be on the order of about once per day over such extended periods, however application rates can vary from about once per week up to about three times per day or more. Improvement of the appearance of dry skin involves topically applying to the skin a safe and effective amount of a composition of the present invention. The amount of the composition which is applied, the frequency of application and the period of use will vary widely depending upon the active levels of a given composition and the level of improvement desired, e.g., in light of the level of dry skin present in the subject.

Improving the appearance of dry skin is preferably practiced by applying a composition in the form of a skin lotion, cream, cosmetic, or the like which is intended to be left on the skin until skin cleansing is appropriate, for some esthetic, prophylactic, therapeutic or other benefit (i.e., a "leave-on" composition). After applying the composition to the skin, it is preferably left on the skin for a period of at least about 15 minutes, more preferably at least about 30 minutes, even more preferably at least about 1 hour, most preferably for at least several hours, e.g., up to about 12 hours.

VIII. EXAMPLES

The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention.

Examples 1-3

A skin cream is prepared by conventional methods from the following components.

	Ingredient (CTFA Name)	Example 1 (Weight %)	Example 2 (Weight %)	Example 3 (Weight %)
PHASE A:	Water U.S.P.	57.31	57.31	57.31
	Disodium EDTA	0.13	0.13	0.13
	Methyl Paraben	0.25	0.25	0.25
	Glycerin	3.00	3.00	3.00
	Zinc Citrate	1.00	1.00	1.00
PHASE B:	Cetyl Alcohol	0.56	0.56	0.56
	Oligomer 1 (as herein described)	0.25	--	--
	Oligomer 12 (as herein described)	--	0.25	--
	Oligomer 18 (as herein described)	--	--	0.25
	Stearyl Alcohol	2.03	2.03	2.03
	Behenyl Alcohol	0.22	0.22	0.22
	Steareth-21 (Brij 721)	0.37	0.37	0.37
	Steareth-2 (Brij 72)	1.10	1.10	1.10
	Distearyldimonium chloride (Varisoft TA-100)	0.95	0.95	0.95
	Propyl Paraben	0.10	0.10	0.10
	Polypropylene glycol-15 stearyl ether (Arlamol E)	3.25	3.25	3.25
PHASE C:	Polypropylene glycol-15 stearyl ether (Arlamol E)	2.17	2.17	2.17
	titanium dioxide	0.75	0.75	0.75
PHASE D:	Niacinamide	5.00	5.00	5.00
	Citric acid	0.19	0.19	0.19
	water U.S.P.	17.00	17.00	17.00
	50% NaOH	0.94	0.94	0.94
PHASE E:	Benzyl Alcohol	0.50	0.50	0.50
	Silicone fluid (DC Q2 - 1401; cyclomethicone/dimethiconol - 50/50 blend	0.75	0.75	0.75
	dimethicone 10 cst	1.00	1.00	1.00
	polyethylene Low Density Beads	1.00	1.00	1.00
PHASE F:	Fragrance	0.10	0.10	0.10
PHASE G:	50% NaOH	0.33	0.33	0.33

Blend the A phase components with a suitable mixer (e.g., Tekmar model RW20DZM), heating while stirring to a temperature of 70-80°C. Separately, blend the B phase components with a suitable mixer and heat with mixing to melt the components. Separately, blend the C phase components and mill to obtain an acceptably smooth mixture (e.g., using a Tekmar T50 Mill).

Add the C phase mixture to the B phase mixture and mix. Then add the resulting mix to the A phase mixture with mixing, cool with a cold water bath and mill, then continue stirring. Remove the combination from the bath, with continued stirring, once the temperature reaches 40°C.

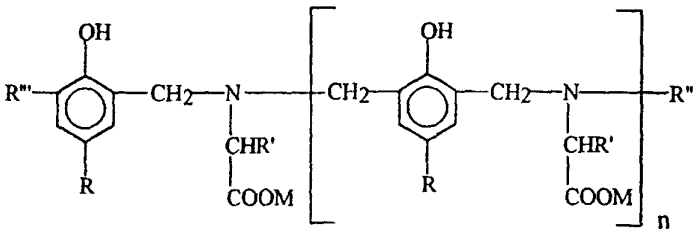
Separately, blend the D phase components by stirring until dissolved, then add this to the combination of A-C materials.

Separately, blend the E phase components by mixing until smooth and continuous, then add this to the combination of the A-D materials. Add and mix the fragrance, then the NaOH. Adjust the pH as necessary to 5.5.

Apply the composition to areas having the appearance of dry skin (e.g., scaliness, crackiness, flakiness) at the rate of 2 mg composition/cm^2 skin once or twice daily for a period of at least 3-6 months to improve the appearance of dry skin.

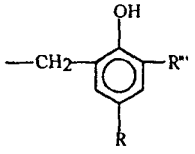
What is claimed is:

1. A skin care compound useful for improving the appearance of dry mammalian skin, characterized in that said compound has the following chemical structure:



wherein

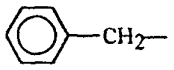
R" is selected from the group consisting of -H or



;

each R is independently selected from the group consisting of C_1-C_{22} alkyl, C_1-C_{22} ester, C_1-C_{22} amide, and C_1-C_{22} ether;

each R' is independently selected from the group consisting of H-, C_1-C_{22} alkyl, HO-CH_2, $CH_3CH(OH)$-, $HSCH_2$-, CH_3-SCH_2CH_2-, H_2NCOCH_2, $H_2NCOCH_2CH_2$-, $HOOCCH_2$-, $HOOCCH_2CH_2$-, and

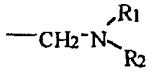


;

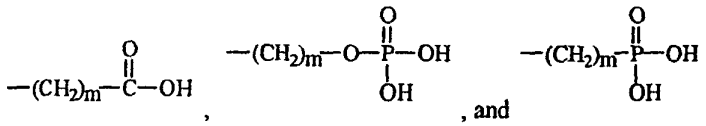
each M is independently selected from the group consisting of H+, C_1-C_{22} alkyl, alkali metal ion, NH_4+, and aluminium ion;

n is an integer from 0 to 6; and

each R''' is independently selected from H or



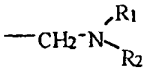
wherein R_1 and R_2 are independently selected from the group consisting of



, and

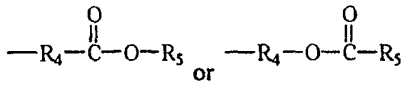
wherein m is an integer from 1 to 3; and

wherein at least one R''' is



if R is a C_1-C_{22} alkyl.

2. A compound according to Claim 1 wherein said C_1-C_{22} ester has the following chemical structure

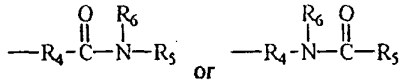


wherein $R_4 + R_5$ equals to C_2-C_{22} ,and wherein

R_4 is selected from the group consisting of straight or branched C_1-C_{18} alkyl, straight or branched C_1-C_{18} alkene, and C_1-C_{18} alkyne, and

R_5 is selected from the group consisting of H, straight or branched C_1-C_{18} alkyl, straight or branched C_1-C_{18} alkene, and C_1-C_{18} alkyne;

said C_1-C_{22} amide has the following chemical structure:

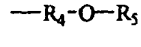


wherein $R_4 + R_5 + R_6$ equals C_2-C_{22}, and wherein

R_4 is selected from the group consisting of straight or branched C_1-C_{18} alkyl, straight or branched C_1-C_{18} alkene, and C_1-C_{18} alkyne, and

R_5 and R_6 are independently selected from the group consisting of H, straight or branched C_1-C_{18} alkyl, straight or branched C_1-C_{18} alkene, and C_1-C_{18} alkyne; and

said C_1-C_{22} ether has the following chemical structure



wherein $R_4 + R_5$ equals to C_2-C_{22}, and wherein

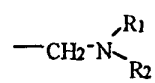
R_4 is selected from the group consisting of straight or branched C_1-C_{18} alkyl, straight or branched C_1-C_{18} alkene, and C_1-C_{18} alkyne, and

R_5 is selected from the group consisting of H, straight or branched C_1-C_{18} alkyl, straight or branched C_1-C_{18} alkene, and C_1-C_{18} alkyne.

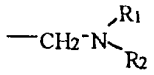
3. A compound according to Claim 1 wherein

R is C_1-C_{22} alkyl; and

R''' is



4. A compound according to Claim 1 wherein
R is C_1-C_{22} ester; and
R''' is H or.



5. A skin care active component comprising a skin care compound according to Claim 1.

6. A skin care active component according to any one of the preceding claims wherein a predominant portion of said skin active component comprises said skin care compound having n equal to or greater than 2.

7. A skin care active component according to any one of the preceding claims wherein said skin active component, which comprises said skin care compound having the specified n values, is obtained by chemical synthetic reaction methods.

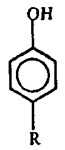
8. A skin care active component according to any one of the preceding claims wherein said skin active component, which comprises said skin care compound having the specified n values, is obtained by employing isolation methods to a reaction product mixture comprising said skin care compound wherein n is an integer from 0 to 6.

9. A topical composition for improving the appearance of dry skin, said composition comprising:
   a) a skin care active component according to Claim 6; and
   b) a dermatologically acceptable carrier.

10. A composition according to Claim 9 further comprising one or more ingredients selected from the group consisting of transparent particles, skin benefit actives, water soluble skin conditioning compounds, structuring agents, anti-inflammatory agents, sunscreens and sunblocks, chelators, desquamation agents, skin lightening agents, and mixtures thereof.

11. A method of synthesizing the compounds according to Claim 1, such method comprising the steps of
(a) reacting formaldehyde with an amino acid at a slightly acidic pH;
(b) adding a cosolvent to the reaction mixture of (a);

(c) adding a C_1 to C_4 alcohol solution of a phenol starting material of the general formula



wherein R is selected from the group consisting of C_1-C_{22} ester, C_1-C_{22} amide, and C_1-C_{22} ether;

(d) heating at reflux with a large molar excess of acetic acid in toluene; and

(e) cooling, separating, and drying the oily layer.

12. A method of synthesizing the compounds according to Claim 1, such method comprising the steps of

(a) obtaining a phenolic hydrophobic metal ion chelator by

(i) reacting formaldehyde with an amino acid at a slightly acidic pH;

(ii) adding a cosolvent to the reaction mixture of (i);

(iii) adding a C_1 to C_4 alcohol solution of a phenol starting material of the general formula

wherein R is selected from the group consisting of C_1-C_{22} alkyl, C_1-C_{22} ester, C_1-C_{22} amide, and C_1-C_{22} ether;

(iv) heating at reflux with a large molar excess of acetic acid in toluene

(v) cooling, separating, and drying the oily layer; and

(b) endcapping the reaction product obtained from synthetic step (a) by

(i) mixing iminodiacetic acid with water and sodium hydroxide and adjusting to a slightly acidic pH;

(ii) adding formaldehyde, sodium hydroxide, and a C_1 to C_4 alcohol to the reaction mixture of step (b)(i) and adjusting to a slightly acidic pH;

(iii) adding the reaction product of Step (a) dissolved in C_1 to C_4 alcohol;

(iv) refluxing the resulting mixture; and

(v) cooling, separating, and drying the oily layer.

13. A method of improving the appearance of dry skin, which method comprises the step of applying to mammalian skin in need of improvement in the appearance of dry skin a safe and effective amount of the composition according to Claim 9.

14. A method of desquamating the skin, which method comprises the step of applying to mammalian skin in need of desquamating a safe and effective amount of the composition according to Claim 9.

15. A method of regulating visible and/or tactile discontinuities in the texture of mammalian skin, which method comprises the step of applying to mammalian skin in need of regulating visible and/or tactile discontinuities in the texture of mammalian skin a safe and effective amount of the composition according to Claim 9.

INTERNATIONAL SEARCH REPORT

Int. tional Application No
PCT/US 99/08183

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/48 C08G14/073

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A61K C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 387 244 A (SCANLON PATRICIA M ET AL) 7 June 1983 (1983-06-07) ---	
A	P.D.HAMPTON ET ALL.: "Synthesis, X-ray structure and alkali-metal binding properties of a new hexahomotriazacalix'3!arene" JOURNAL OF THE CHEMICAL SOCIETY, PERKIN TRANSACTIONS 2., no. 6, June 1996 (1996-06), pages 1127-1130, XP002112541 CHEMICAL SOCIETY. LETCHWORTH., GB ISSN: 0300-9580 abstract ---	
A	US 4 655 949 A (LANDRY JAMES F ET AL) 7 April 1987 (1987-04-07) example 1 -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 August 1999	01/09/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Stienon, P

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int tional Application No
PCT/US 99/08183

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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